

Upper Atmosphere

Program

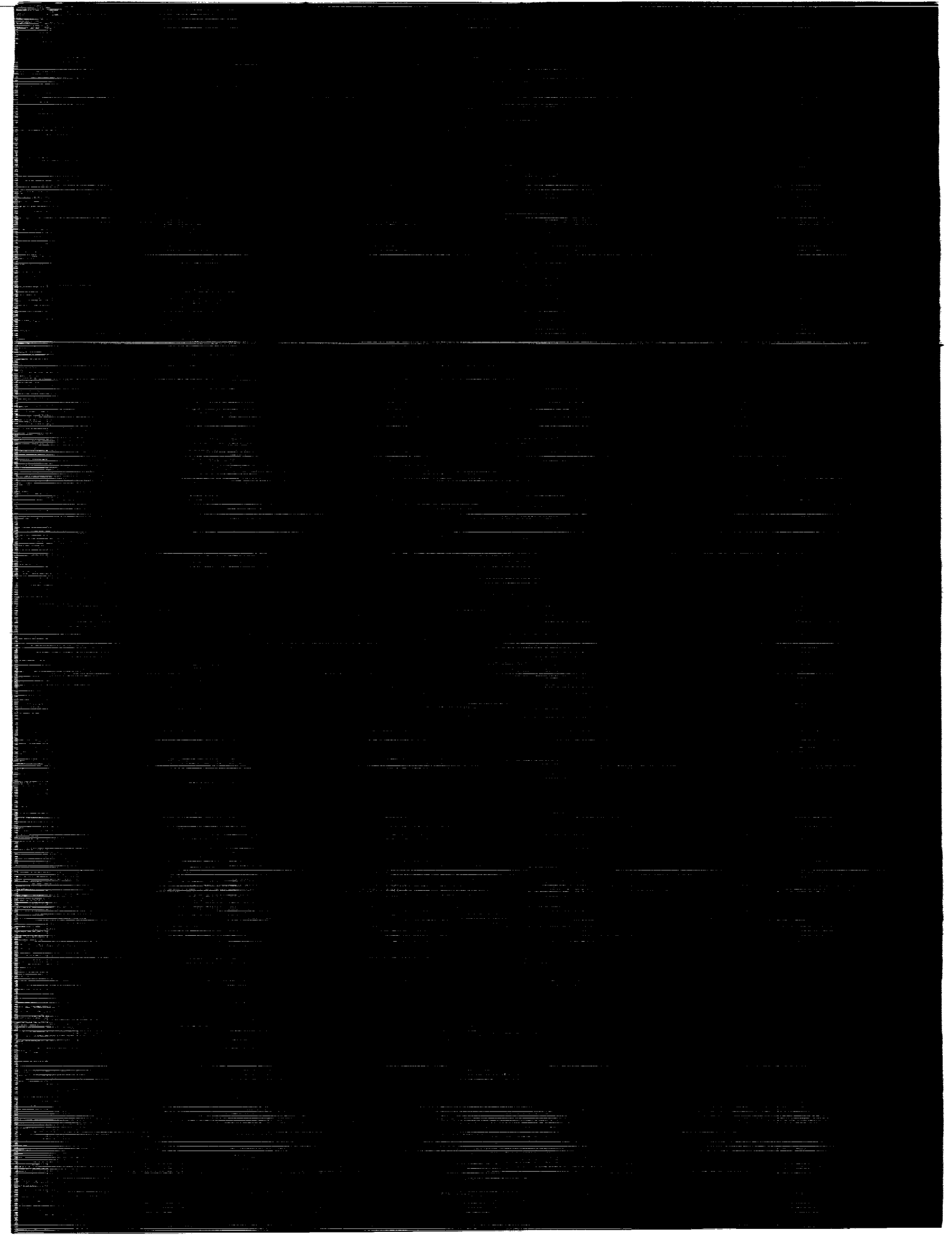
Summaries

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NASA Upper Atmosphere
Research Program:

Research Summaries

1988-1989

**Report to the Congress and the
Environmental Protection Agency
on the National Aeronautics and Space Administration
Upper Atmosphere Research Program**

January 1990



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Washington, D.C. 20546

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INTRODUCTION

INTRODUCTION

In compliance with the Clean Air Act Amendments of 1977, P. L. 95-95, the National Aeronautics and Space Administration (NASA) has prepared a report on the state of our knowledge of the Earth's upper atmosphere, particularly the stratosphere, and on the progress of the NASA Upper Atmosphere Research Program (UARP). The report is composed of two parts. Part I is the present document, which summarizes the objectives, status, and accomplishments of the research tasks supported under the NASA UARP. Part II is an assessment entitled "Present State of Knowledge of the Upper Atmosphere: An Assessment Report", which will be issued in March, 1990. It consists primarily of the Executive Summary and Chapter Summaries of the World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 20, "Scientific Assessment of Stratospheric Ozone: 1989", sponsored by NASA, the National Oceanic and Atmospheric Administration, the U.K. Department of the Environment, the United Nations Environment Program, and the World Meteorological Organization. Other sections of Part II include: (a) the Executive Summary of the Alternative Fluorocarbon Environmental Acceptability Study Report, (b) a report entitled "Transient Scenarios for Atmospheric Chlorine and Bromine", (c) a modeling analysis of the effects of chlorine emissions from Space Shuttle operations on stratospheric ozone, and (d) the most recent evaluation of the photochemical and chemical kinetics data which are used as input parameters for the atmospheric models.

Under the mandate contained in the FY 1976 NASA Authorization Act, NASA has developed and is implementing a comprehensive program of research, technology, and monitoring of the Earth's upper atmosphere, with emphasis on the stratosphere. This program focuses on expanding our understanding of this important region of our atmospheric environment, and on developing an ability to assess potential perturbations, particularly to the ozone layer. The NASA UARP is managed within the Earth Science and Applications Division in the Office of Space Science and Applications. The long-term objectives of the present program are to perform research to:

- a. understand the physics, chemistry and transport processes of the upper atmosphere, and
- b. accurately assess possible perturbations of the upper atmosphere caused by human activities as well as by natural phenomena.

The NASA program supports a variety of research tasks proposed by scientists from the university, government, and industrial research communities. The UARP also sponsors periodic assessments of the state of our knowledge of the upper atmosphere and its response to specific perturbations such as chlorofluoromethane (CFM) releases, aircraft effluents, and other potential pollutants. Of greatest urgency at present is an assessment of the combined effects of continued increases in the atmospheric concentrations of CFCl_3 , CF_2Cl_2 , CH_3CCl_3 , CF_3Br , CF_2ClBr , and other halocarbons, CO_2 , NO_x , and other gases such as N_2O and CH_4 . Another goal is to understand the role of stratospheric ozone in the radiative heating and dynamics of the atmosphere and, thereby, to assess the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere. Other tasks involve the analysis of data obtained by large satellite missions such as SAGE I and II and Nimbus-7, and by aircraft campaigns such as the Stratosphere Troposphere Exchange Project (STEP), the Airborne Antarctic Ozone Experiment (AAOE), and the Airborne Arctic Stratospheric Expedition (AASE). In addition, it supports laboratory and field measurement activities in preparation for the analysis and interpretation of data from the Upper Atmosphere Research Satellite (UARS) scheduled for launch in the Fall of 1991. In the portion of the program other than direct satellite missions, activities fall into four broad categories: (1) field measurements

(employing in-situ and remote sensing techniques from ground-based, aircraft, balloon, and rocket platforms); (2) laboratory studies (gas phase and heterogeneous kinetics, photochemistry, spectroscopy, and calibration standards development); (3) theoretical studies (1-D, 2-D, and 3-D models of photochemistry and dynamics); and (4) data analysis (especially analyses of large satellite data sets). Funding of the research program was \$27.0M in FY 89. Since the 1988 report, substantial advances in our knowledge of the upper atmosphere have been made in each of the four major research categories. Laboratory studies have strengthened our knowledge of the chemical kinetics of stratospheric components, and have provided improved data on the spectroscopy of atmospheric gases for applications to atmospheric measurements of trace species. Many of the trace gases in the hydrogen, nitrogen, and chlorine chemical families which participate in the chemistry of ozone have been detected in the stratosphere, and detailed information on their spatial and temporal variations is becoming more available. Current research funding supports specific investigations dealing with the following topics:

- a. Determination of the distribution of trace gases in the upper atmosphere, with emphasis on those species which influence the ozone balance.
- b. Observations of the global distribution of ozone, its vertical profile, and temporal variations. A key initiative in this area is the implementation of a ground-based remote-sensing measurement Network for the Detection of Stratospheric Change (NDSC).
- c. Determination of the geographic distribution and strengths of the sources and sinks for stratospheric compounds. A strong focus in this area is associated with chlorofluorocarbon alternatives, namely the hydrochloro-fluorocarbons (HCFCs).
- d. Development of more realistic multi-dimensional models of the stratosphere and troposphere.
- e. Application of 2-D and 3-D stratospheric models to assess the impacts of changing atmospheric composition. Specific emphasis is being placed on assessing the impact of high speed aircraft on stratospheric ozone and chemistry.
- f. Utilization of theoretical models to develop a strategy for detecting change in atmospheric ozone.
- g. Improvements in the understanding of atmospheric dynamics and transport processes by both theory and measurement.
- h. Validation of theoretical models by comparison with atmospheric measurements.
- i. Measurements of the ultraviolet solar irradiance and its temporal variations.
- j. Determination of the mechanisms responsible for exchange of air between the troposphere and stratosphere.
- k. Laboratory studies in spectroscopy and chemical kinetics relevant to the interpretation of atmospheric measurements and to theoretical simulations of the atmosphere.

1. Development of new technological ideas, techniques, and instruments for use in upper atmospheric research.

There are several activities during 1988 and 1989 that should be highlighted. In general, they each involved an integration of several facets of the research supported by the UARP. These include:

1. **An extended analysis of the data from the Airborne Antarctic Ozone Experiment conducted in late 1987.** This analysis established a direct cause and effect relationship between the Antarctic Ozone Hole and chlorine liberated from man-made chlorofluorocarbons.
2. **The 1989 Airborne Arctic Stratospheric Expedition.** This measurement campaign found that the chemical composition of the Arctic polar stratosphere was highly perturbed in a manner similar to that which had been observed during the Antarctic spring. While no unequivocal signature of photochemical loss of Arctic ozone was identified, by the end of the mission a considerable portion of the vortex air was primed for ozone destruction. These results have substantially increased confidence in the scientific understanding of the polar stratospheric cloud induced, chlorine catalyzed ozone depletion phenomenon. As a result, it is clear that enhancements of chemically active chlorine compounds do indeed occur in both the Arctic and Antarctic stratosphere.
3. **A reanalysis of total column ozone data.** Several recent analyses of total column ozone data from ground-based Dobson instruments support the conclusion of the 1988 International Ozone Trends Panel (OTP) that there is a downward trend in ozone during winter at mid-to-high latitudes in the Northern Hemisphere over the past two decades. The extension of the data set beyond that used by the OTP to include 1987 and 1988 does not alter the basic conclusions regarding trends in winter. In addition, no statistically significant zonal trends were found for the summer period (May - August) through 1988. Lastly, within longitudinal sectors, regional differences in the ozone trends were indicated in the Northern Hemisphere, i.e., with the largest changes being observed over North America and Europe and the smallest over Japan. A new internal calibration technique has been developed for analyzing data from the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus-7 satellite. This technique has the capability of maintaining an accuracy of 1% over a 10-year period. Reanalysis of the 10-year data record (through 1988) by this technique agrees with the trends determination derived from the ground-based Dobson network.
4. **Completion of the latest international assessment of stratospheric ozone.** NASA and the National Oceanic and Atmospheric Administration (NOAA) coordinated the "Scientific Assessment of Stratospheric Ozone: 1989" co-sponsored by the United Nations Environment Program, the World Meteorological Organization, and the United Kingdom Department of Environment. This assessment was one of four conducted under the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer. It serves as the scientific basis for assessing and modifying the control measures of the Protocol.

5. **Implementation of the Network for the Detection of Stratospheric Change (NDSC).** An international meeting formally establishing the organizational structure of the NDSC was held in Geneva, Switzerland, in November of 1989. The Network is a set of high quality research stations for observing and understanding changes in the physical and chemical state of the stratosphere that are complemented by secondary stations and satellite measurements and are coordinated with other networks. The NASA UARP (together with NOAA and the Chemical Manufacturers Association) have been supporting the development of the state-of-the-art instrumentation with which such stations will be equipped. The newly formed NDSC Steering Committee and Science Team will focus on many operational issues such as site selection, instrument evaluation and calibration, data analysis and archiving, etc. It is anticipated that some of the NDSC stations will be operational in time to provide complementary and correlative measurements for the Upper Atmosphere Research Satellite. A fully implemented NDSC will serve as a focal point for future ozone trends determinations.

I. FIELD MEASUREMENTS

- A. BALLOON-BORNE IN-SITU MEASUREMENTS
- B. BALLOON-BORNE REMOTE MEASUREMENTS
- C. GROUND-BASED MEASUREMENTS
- D. AIRCRAFT-BORNE MEASUREMENTS
- E. ROCKET-BORNE MEASUREMENTS
- F. INSTRUMENT DEVELOPMENT

A. BALLOON-BORNE IN-SITU MEASUREMENTS

Measurement of Trace Stratospheric Constituents with a Balloon Borne Laser Radar

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Co-Investigator Thomas J. McGee

The objective of this research has been to measure the concentration of stratospheric hydroxyl radical and related chemical species as a function of altitude, season, and time of day. Although hydroxyl plays a very important role in the chemistry controlling stratospheric ozone little is known about its behavior because it has been a difficult species to measure. The instrument employed in this program was a laser radar employing the technique of remote laser induced fluorescence. This instrument offers a number of attractive features including extreme specificity and sensitivity, a straightforward relationship between observed quantity and the desired concentration, and immunity to self-contamination.

The instrument was flown three times in the FY88-FY89 time period--June 1988, September 1988, and June, 1989. Additionally in early FY88 a modified instrument operated from the ground measuring ozone at McMurdo, Antarctica as part of the NOZE II expedition to investigate the south polar "ozone hole." All three of the flights obtained high quality measurements of the diurnal variation of hydroxyl radical and the September flight observed the transition through sunset when the concentration of hydroxyl plummets as the principal formation mechanisms for the radical cease. Analysis of the results of all three flights is continuing at present although a preliminary presentation of the data was made at the Fall 1988 meeting of the AGU. Unfortunately the instrument was lost in a freak accident during the June, 1989 flight. The instrument was overflying a severe thunderstorm and suffered a "free fall" from an altitude of roughly 105,000 feet. The mechanism for the accident is currently under investigation; lightning is implicated at the present time.

The following recent publications have arisen from this research:

John Burris, William S. Heaps, and John Cavanaugh, Ground Based Lidar Measurements of Antarctic Ozone in 1987, submitted to JGR.

William S. Heaps, James Butler, and T. J. McGee, Hydroxyl Radical Concentration Profiles in the Middle Stratosphere, in preparation.

IN SITU MEASUREMENTS OF STRATOSPHERIC OZONE

Principal Investigator: J. J. Margitan
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Dr.
Pasadena, CA 91109

Co-Investigator: M. H. Proffitt
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325 Broadway
Boulder, CO 80303

Objective:

Under this task, the stratospheric abundance of ozone is measured using an in situ UV absorption instrument flown piggyback aboard balloon flights launched from NSBF. The dual channel UV photometer obtains ozone profiles on ascent and descent with 1-10 second time resolution (5-50 meters) with an accuracy of 3%. These measurements aid in understanding the distribution of ozone in the stratosphere, particularly the upper stratosphere near 40 km, as well as providing complementary and comparative data for other instruments.

Results:

There have been three recent flights of the UV photometer, which is shown in Figure 1. The first flight of the instrument, with its new command, timing, and data handling system was on September 13, 1988 at Palestine Texas (32°N, 96°W) aboard the gondola carrying the JPL BLISS (Balloon-borne Laser In Situ Sensor) instrument. The UV and BLISS ozone measurements are compared in Table 1.

Table 1. Comparison of BLISS and UV Ozone Mixing Ratios (ppmv)

Time (CDT)	P mb	Retro (m)	BLISS O ₃	UV O ₃
1635	11.21	100	8.24	8.25
1735	11.15	100	8.26	8.27
0045	10.37	200	8.52	8.30
0605	11.21	200	8.13	8.15
1150	6.58	200	9.03	8.55
1210	6.58	100	9.21	8.61

A second flight of the UV ozone photometer was made on May 27, 1989 aboard the BMLS (Balloon Microwave Limb Sounder) gondola, again from Palestine. In Figure 2, the UV ozone profile is compared with the (preliminary) values derived from the BMLS retrieval, the profile retrieved as a 30°N zonal average by the shuttle borne

ATMOS instrument in May 1985, and a recent model calculation by Natarajan and Callis (Geophys. Res. Lett. 16, 473, 1989) using the trace gas distributions measured by ATMOS. The agreement among observations and model in the 35-40 km range stands in sharp contrast to the situation which has existed for the last few years (both WMO 1985 and NASA 1988) where the values accepted for observed ozone (principally SBUV and LIMS) seemed to lie 30-50% higher than model calculations above 35 km.

A third flight of the instrument was made from Palestine on August 29, 1989 aboard the UV spectrometer of the University of Liege which was measuring OH via UV solar absorption.

Publications:

J. J. Margitan, G. A. Brothers, E. V. Browell, D. Cariolle, M. T. Coffey, J. C. Farman, C. B. Farmer, G. L. Gregory, J. W. Harder, D. J. Hofmann, W. Hypes, S. Ismail, R. O. Jakoubek, W. Komhyr, S. Kooi, A. J. Krueger, J. C. Larsen, W. Mankin, M. P. McCormick, G. H. Mount, M. H. Proffitt, A. R. Ravishankara, A. L. Schmeltekopf, W. L. Starr, G. C. Toon, A. Torres, A. F. Tuck, A. Wahner and I. Watterson, "Intercomparison of Ozone Measurements Over Antarctica", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

M. H. Proffitt, J. A. Powell, A. F. Tuck, D. W. Fahey, K. K. Kelly, A. J. Krueger, M. R. Schoeberl, B. L. Gary, J. J. Margitan, K. R. Chan, M. Loewenstein and J. R. Podolske, "A Chemical Definition of the Boundary of the Antarctic Ozone Hole", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

A. F. Tuck, R. T. Watson, E. P. Condon, J. J. Margitan and O. B. Toon, "The Planning and Execution of ER-2 and DC-8 Aircraft Flights Over Antarctica, August and September 1987", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

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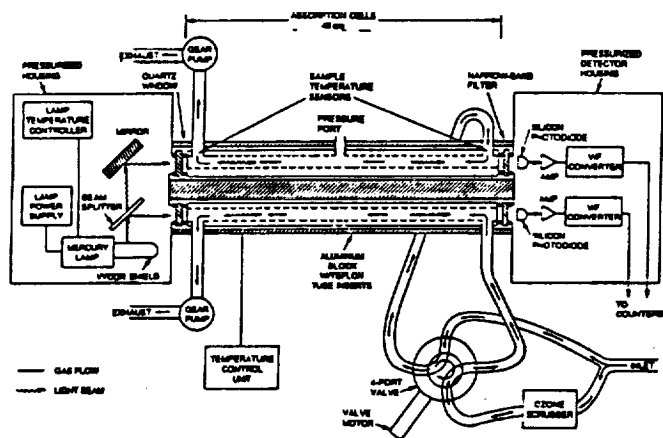
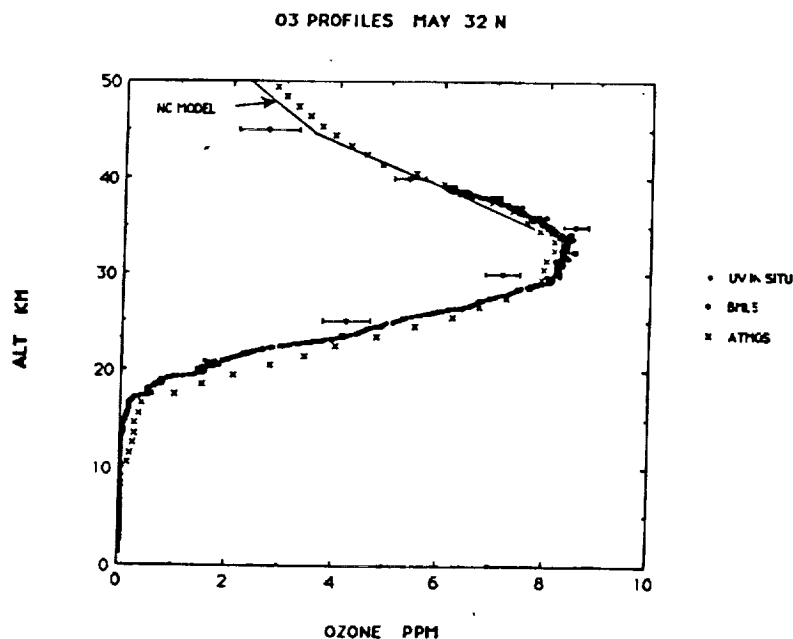


Figure 1. Schematic diagram of the instrument.



UV and BMLS measurements of ozone on the flight of May 27, 1989, compared to the ATMOS 30 N zonal average measured in May 1985, and a recent model calculation by Natarajan and Callis.

A. Neutral Constituent Measurement in the Stratosphere

B. Principal Investigator: Konrad Mauersberger
School of Physics and Astronomy
University of Minnesota
Minneapolis, MN 55455

C. Abstract of Research Objectives:

The research objectives are: Measurements of major and minor neutral constituents in the middle and upper stratosphere using a mass spectrometer or sample collection system. Laboratory studies of ozone's chemical and physical properties, the enhancements of ozone's heavy isotopes. Calibration of instruments using an absolute ozone calibration system. Laboratory studies simulating polar stratospheric cloud particles, condensation of nitric acid trihydrates (NAT), solubility of HCL in ice and NAT's.

D. Summary of Progress and Results:

The observed unusual enhancement in the heavy isotopes of stratospheric ozone found by mass spectrometer and infrared instrument measurements has been studied in a variety of laboratory experiments using mass spectrometers and tunable diode lasers. Enhancements at mass 50 of about 15% have been repeatedly measured. In a unique experiment all isotopes of ozone were formed (48 through 54) and the enhancements measured: A clear dependence on the symmetry of the ozone molecule was found. Ozone of mass 51 ($^{16}\text{O}^{17}\text{O}^{18}\text{O}$), representing a complete asymmetric molecule, showed an enhancement of 20%. A number of theories to explain the ozone isotopic results have been tested in those laboratory studies. So far, results have shown that during the ozone formation process $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ the isotopic fractionation occurs. An understanding of the isotope enrichment process will provide information on the formation of the ozone molecule.

Extensive laboratory studies have been conducted to experimentally test the formation and composition of polar stratospheric cloud particles which play an important role in the large ozone reduction observed during Spring. For the first time, we measured in a lab simulation experiment the temperature of formation and the composition of the cloud particles: HNO_3 and H_2O condense above ice temperature to form nitric acid trihydrates (NATs) which may be diluted by additional ice condensation as the temperature drops below the ice point. In addition the solubility of HCL in ice and NAT's was investigated and it was found that the solubility of HCL in ice is low, it is, however,

much higher in NATs. Surface effects on cloud particles may play a major role in the heterogeneous chemistry.

A new collection system has been designed and flown on board a balloon gondola to obtain, besides others, ozone samples in the stratosphere. Samples are returned to the laboratory for precision analysis of ozone isotopes, including the isotopic ratio for mass 49. The first flight was successful and provided isotopic ratios showing an enhancement similar to those found with other techniques. Data from a second successful flight are being analyzed at the present time.

E. Journal Publications:

1. "Vapor Pressures of $\text{HNO}_3/\text{H}_2\text{O}$ at Low Temperatures," D. Hanson and K. Mauersberger, J. Phys. Chem. **92**, 6167 (1988).
2. "Laboratory Studies of the Nitric Acid Trihydrate: Implications for the South Polar Stratosphere," D. Hanson and K. Mauersberger, Geophys. Res. Lett. **15**, 855-858 (1988).
3. "Solubility and Equilibrium Vapor Pressures of HCL Dissolved in Polar Stratospheric Cloud Materials: Ice and the Trihydrate of Nitric Acid", D. Hanson and K. Mauersberger, Geophys. Res. Lett. **15**, 1507-1510 (1988).
4. "Laboratory Studies of Heavy Ozone," J. Barnes, B. Schueler, J. Morton, and K. Mauersberger, accepted for publication, JGR (1989).
5. "Oxygen Fractionation of Ozone Isotopes $^{48}\text{O}_3$ Through $^{54}\text{O}_3$ ", J. Morton, B. Schueler, and K. Mauersberger, Chem. Phys. Lett. **154**, 143-145 (1989).
6. "Laboratory Measurements of Ozone Isotopomers by Tunable Diode Laser Absorption Spectroscopy", S.M. Anderson, J. Morton, and K. Mauersberger, Chem. Phys. Lett. **156**, 175-180 (1989).
7. "HCL/ H_2O Solid Phase Vapor Pressures and HCL Solubility in Ice", D. Hanson and K. Mauersberger, submitted to J. Phys. Chem. (1989).

BALLOON-BORNE LASER IN-SITU SENSOR (BLISS)
AIRCRAFT LASER INFRARED ABSORPTION SPECTROMETER (ALIAS)

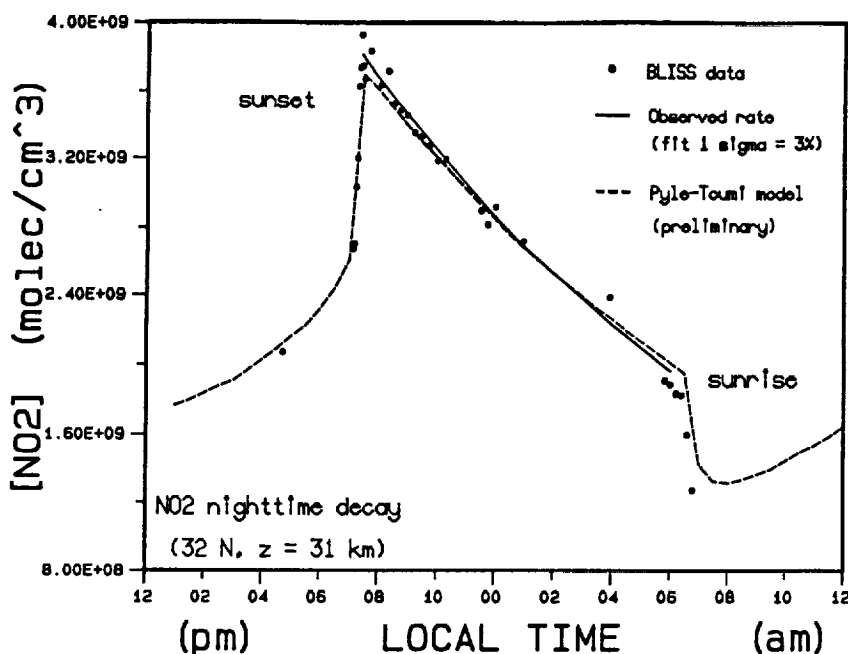
Principal Investigator: Dr. Christopher R. Webster
Co-Investigator: Dr. Randy D. May
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Abstract of Research Objectives

The Balloon-borne Laser In-Situ Sensor (BLISS) and the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) programs have as their primary objective the collection of reliable data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere. The BLISS instrument uses tunable diode lasers in the 4 to 20- μ m wavelength region to measure the absorption due to selected species between the balloon gondola and a lowered retroreflector which defines a path of up to 1 km. The current measurement capability for a single flight includes: NO, NO₂, O₃, HNO₃, CH₄, HCl, H₂O, N₂O, CO₂, and jNO₂ (Stedman), with capability for more species.

Summary of Progress and Results

The BLISS instrument was successfully flown twice in 1988 from Palestine, Texas. Simultaneous in-situ measurements of [NO], [NO₂], [HNO₃], [O₃], [CH₄], [N₂O], jNO₂, pressure, and temperature at 30 km were made on Sept. 13, 1988 with BLISS carrying piggy-back two other instruments: a NOAA dual-channel balloon UV Ozone Spectrometer, and the U. of Denver upward- and downward-looking radiometers for measurement of jNO₂. Using tunable diode laser absorption spectroscopy over a long pathlength, measurements were made of daytime [NO], [NO₂], [O₃], with supporting jNO₂, and of the diurnal variation in [NO₂]. Measurements of [NO₂], made every half-minute throughout much of the night, show the NO₂ mixing-ratio falling from a sunset value of 10.5 ppbv to about 5 ppbv at night's end. According to the simple identity $(d/dt)[NO_2] = -2k[NO_2][O_3]$ for the rate of decay of [NO₂], where k is the rate constant for the reaction between NO₂ and O₃, an exponential fit to the observed decay agrees with the decay rate calculated using in-flight measured O₃ concentrations and the laboratory-measured rate constant to about 7%, with a one-sigma standard deviation of the fit of only $\pm 3\%$. Photochemical model calculations constrained to the measured temperature and ozone values, and incorporating both N₂O₅ and ClONO₂ chemistry, predict in detail the observed NO₂ diurnal behavior. From the sunset/sunrise difference in the volume mixing ratio of NO₂ is derived a value of 2.75 ppbv for the sunrise N₂O₅ mixing-ratio,



Diurnal variation of $[\text{NO}_2]$
at 30 km and 32°N measured
by BLISS instrument.

Derived N_2O_5 vmr = 2.75 ppbv

in excellent agreement with the model prediction of 2.78 ppbv at this latitude. Simultaneous measurements of the mixing ratios of HNO_3 and post-sunset NO_2 , allow an estimate of total odd nitrogen, approximated by $[\text{NO}_2] + [\text{HNO}_3] + 2[\text{N}_2\text{O}_5]$, of 15.8 ± 0.7 ppbv at 30 km. The OH concentration derived from the measured $[\text{NO}_2]/[\text{HNO}_3]$ ratio is compared with previous direct measurements.

In the May 1988 flight, in addition to studies of odd-nitrogen photochemistry, an intercomparison of BLISS-measured HCl was made with R. Zander's U. of Liege instrument, on another balloon at the same time (see ref. 1).

The build of the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) experiment for the ER-2 began in October 1988, with BLISS balloon flights suspended for one year. This instrument will measure NO_2 , HNO_3 , HCl, CH_4 , O_3 , and H_2O on future polar missions. The design is completed, and the build underway, with plans to integrate the instrument at NASA Ames in July 1990.

E. Journal Publications

1. "In-situ Stratospheric Measurements of HNO_3 and HCl near 30 km using the BLISS Tunable Diode Laser Absorption Spectrometer", R. D. May and C. R. Webster, accepted for publication, Geophys. Res. Letters, 1989.
2. "Simultaneous In-situ Measurements of NO, NO_2 , HNO_3 , O_3 , N_2O , and jNO_2 using the BLISS Diode Laser Spectrometer: the Daytime NO_2/NO Ratio, the Nighttime Decay of NO_2 , Derived N_2O_5 and OH, and Estimate of NO_y at 30 km", C. R. Webster, R. D. May, R. Toumi, J. Pyle, and D. Stedman, prepared for submission to JGR, 1989.
3. "Stratospheric Measurements of Isotopic CH_4 , N_2O , and CO_2 using the BLISS Tunable Diode Laser Spectrometer", C. R. Webster and R. D. May, in preparation for Geophys. Res. Letters, 1989.

A. Balloon-Borne and Aircraft-Borne, In Situ Measurements of Stratospheric Free Radicals

B. James G. Anderson, Harvard University

C. Abstract. Free radicals from the chlorine, bromine, hydrogen, oxygen and nitrogen families constitute the catalytic chain sustaining species which dictate chemical transformation rates in the stratosphere and troposphere. This research is directed toward *in situ* detection of OH, HO₂, Cl, ClO, BrO, O₃ and H₂O from balloons and from the ER-2 aircraft. The scope of the work embraces balloon and aircraft field programs, instrument development, data analysis, and interpretation based on photochemical calculations. Isolating and quantifying ozone destruction mechanisms in the midlatitude and polar stratospheres is the abiding objective.

D. Progress and Results

1. Detection of OH and HO₂ using the high repetition rate copper vapor laser. We report on three flights of the copper vapor laser system: 15 July 1987, 6 July 1988, and 25 August 1989. Figure 1 displays the results of the first two flights which define for the first time the hydroxyl radical concentration in the most critical region of the stratosphere, 22-40 km altitude. Figure 2 displays the high time resolution OH and HO₂ data in the lower-middle stratosphere, obtained on 25 August 1989, representing the first simultaneous, *in situ* spectroscopic measurements of OH and HO₂ in the critical altitude region. While these results are discussed in detail in the manuscripts listed under E, it is clear that the observed OH distribution occupies the lower boundary of the OH distribution predicted by current models, indicating that OH is controlled at and below 30 km by HONO₂ and HO₂NO₂.

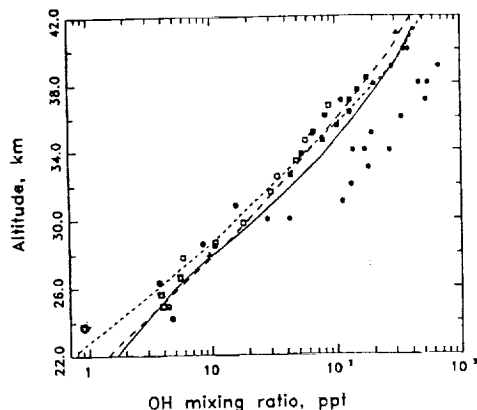


Figure 1

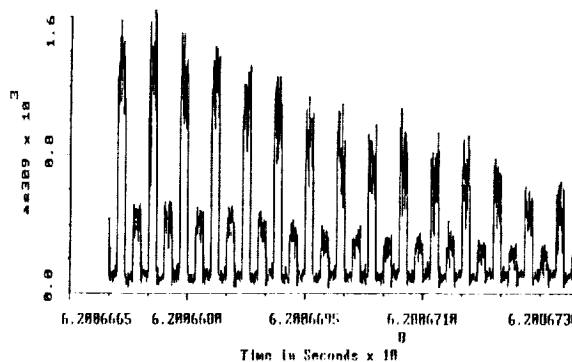


Figure 2

2. Simultaneous detection of OH, HO₂, H₂O, and O₃ from the multisensor balloon package. Figure 3 notes the geometry of the balloon gondola, and Figure 4 reviews the simultaneously observed profiles of OH, H₂O, and O₃ obtained from the instrument array on 6 July 1988.

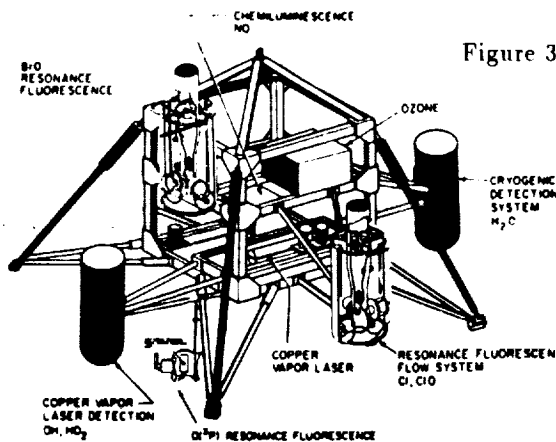


Figure 3

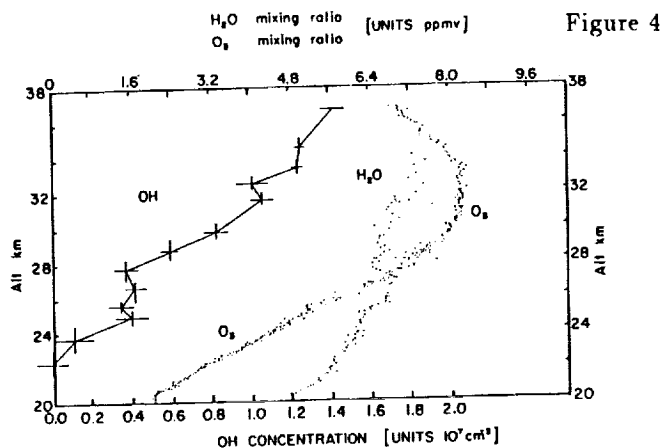


Figure 4

3. ClO and BrO detection from the ER-2 aircraft within the Antarctic and Arctic vortices. A significant fraction of our field efforts turned toward aircraft missions into the polar regions; specifically the AAOE and AASE projects that demonstrated that CFCs were responsible for the Antarctic ozone hole. Figures 5 and 6 trace the development of O₃ anticorrelation from the initial conditions on 23 August 1987 to 16 September 1987 within the Antarctic vortex. A detailed analysis of the kinetics of ozone destruction by ClO and BrO, both observed *in situ* simultaneously with

O₃, demonstrates that a major fraction of the observed rate of O₃ loss can be accounted for by currently proposed mechanisms, but that there may be other contributions.

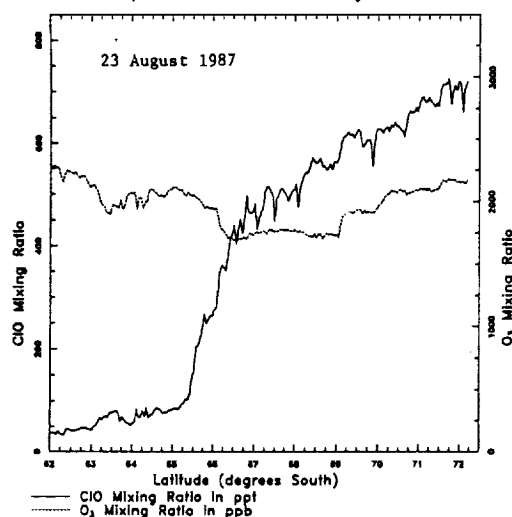


Figure 5

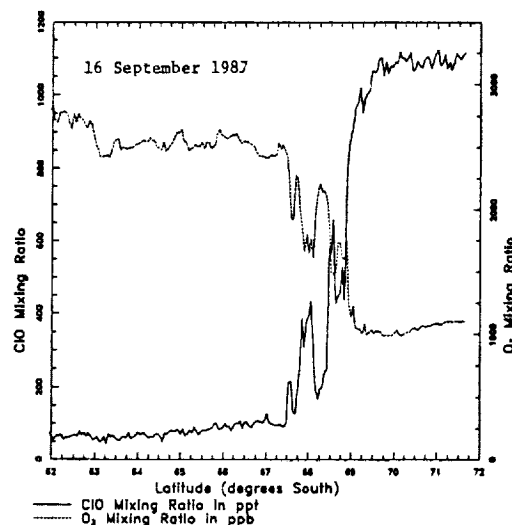


Figure 6

Finally, two flight series were made into the Arctic, the first a single flight to the edge of the Arctic vortex in February, 1988, and the second an extensive series as part of the AASE mission to Stavanger, Norway in January–February, 1989. As was the case for the Antarctic, extremely high CIO concentrations were observed, as shown in Figure 7.

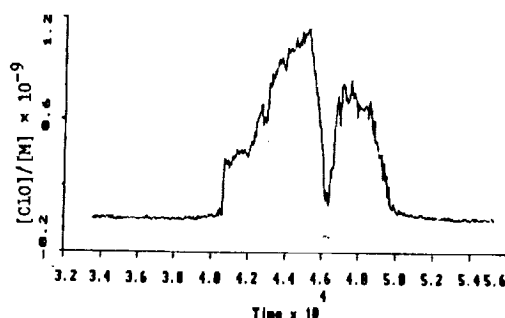


Figure 7

E. Journal Publications

1. Anderson, J. G., "Free radicals in the Earth's atmosphere: Their measurement and interpretation," *Ann. Rev. Phys. Chem.* **38**, 489–520, 1987.
2. Brune, W. H., E. M. Weinstock, and J. G. Anderson, "Midlatitude CIO below 22 km altitude: measurements with a new aircraft-borne instrument," *Geophys. Res. Lett.* **15**(2), 144–147, 1988.
3. Brune, W. H., D. W. Toohey, J. G. Anderson, W. L. Starr, J. F. Vedder, and E. F. Danielsen, "In situ observations of CIO and O₃ in the wintertime lower stratosphere between 37°N and 61°N latitude," *Science* **242**, 558–562, 1988.
4. Stimpfle, R. M., and J. G. Anderson, "In situ detection of OH in the lower stratosphere with a balloon borne high repetition rate laser system," *Geophys. Res. Lett.* **15**(13), 1503–1506, 1988.
5. Anderson, J. G., W. H. Brune, S. A. Lloyd, D. W. Toohey, S. P. Sander, W. L. Starr, M. Loewenstein, and J. R. Podolske, "Kinetics of O₃ destruction by CIO and BrO within the Antarctic vortex: An analysis based on *in situ* ER-2 data," *J. Geophys. Res.*, in press, 1989.
6. Anderson, J. G., W. H. Brune, and M. H. Proffitt, "Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of CIO–O₃ anticorrelation based on *in situ* ER-2 data," *J. Geophys. Res.*, in press, 1989.
7. Brune, W. H., J. G. Anderson, and K. R. Chan, "In situ observations of CIO in the Antarctic: ER-2 aircraft results from 54°S to 72°S latitude," *J. Geophys. Res.*, in press, 1989.
8. Brune, W. H., J. G. Anderson, and K. R. Chan, "In situ observations of BrO over Antarctica: ER-2 aircraft results from 54°S to 72°S latitude," *J. Geophys. Res.*, in press, 1989.
9. Stimpfle, R. M., L. B. Lapson, and J. G. Anderson, "Balloon borne *in situ* detection of OH in the stratosphere from 37 to 23 km," *Geophys. Res. Lett.*, in press, 1989.

Measurements of Nitric Oxide and Total Odd Nitrogen in the Stratosphere

A.J. Weinheimer, J.D. Shetter, J. Walega, F. Grahek, B.A. Ridley

National Center for Atmospheric Research, Boulder, CO 80307 *

Objectives

The nitric oxide instrument is designed for flight on the Harvard University (Professor J. G. Anderson) gondola. The NO measurement accompanies a suite of other measurements of radical species (HO , HO_2 , Cl , ClO , O) that are believed to control the abundance of stratospheric ozone. By measuring these species simultaneously, theoretical predictions of stratospheric photochemistry may be tested.

The total odd nitrogen instrument is a stand-alone experiment designed to provide critical information concerning the modelled impact of future anthropogenic emissions of chlorine-containing species upon stratospheric ozone. Current estimates of total odd nitrogen rely upon summing measurements—along with all the associated uncertainties—of individual species. This experiment should provide data of sufficient accuracy to narrowly restrict models of the stratospheric odd nitrogen budget.

Progress

The nitric oxide instrument has undergone further testing, modification, and calibration. An ultraviolet absorption cell has been added for monitoring the ozone used to produce chemiluminescence in the measurement of NO. The instrument was tested in a high-altitude chamber, where it functioned extremely well, except for a design flaw in the mass flow controllers that was discovered as a result of these tests. The controllers exhibit a marked variation in sensed (and hence controlled) flow with a variation in ambient pressure, in violation of the manufacturer's specifications. This was overcome by housing the controllers in a pressure-tight box. The instrument was flown on the Harvard gondola on July 28, 1989. Unfortunately, the instrument's data acquisition system failed during the flight, resulting in the acquisition of virtually no scientific data. This was not as tragic as it might have been, for the Harvard gondola failed to acquire the desired data on OH and HO_2 . Fortunately, some useful information on the instrument's performance in the stratospheric environment has been obtained from the housekeeping signals, and this will lead to improvements prior to the next flight.

* The National Center for Atmospheric Research is sponsored by the National Science Foundation.

The total odd nitrogen instrument utilizes an inlet converter on the nitric oxide instrument to reduce NO_2 , HNO_3 , N_2O_5 , ClONO_2 , etc., to NO . The inlet converter has been thoroughly bench-tested to characterize the pressure, temperature, humidity, reducing reagent (H_2 or CO), and O_3 effects on the conversion of NO_2 , HNO_3 , and NH_3 to NO . The most notable operational difference between ground- and aircraft-based converters and the balloon-based converter is the need to operate the balloon device at constant pressure. This means the converter will be mounted downstream of the existing inlet valve and the inlet valve will need to be tested to determine its ability to pass the various components of NO_y . No difficulties are anticipated. The existing payload needs to be modified to accommodate the additional hardware required for NO_y measurement. This includes the CO cylinder, regulator, and flow controller; the NO_y calibration source; as well as the batteries and temperature controller for the converter.

B. BALLOON-BORNE REMOTE MEASUREMENTS

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TITLE OF RESEARCH TASK: Infrared Measurements of Atmospheric Constituents

INVESTIGATORS: David G. Murcray, Physics Department, University of Denver
 Frank J. Murcray, Physics Department, University of Denver
 Aaron Goldman, Physics Department, University of Denver
 Curtis P. Rinsland, NASA Langley Research Center
 C. Camy-Peyret, Lab. de Phys. Moleculaire et Atmospherique
 J.M. Flaud, Lab. de Phys. Moleculaire et Atmospherique

ABSTRACT OF RESEARCH OBJECTIVES:

The objective of this program is to obtain data concerning the concentration versus altitude of various constituents of interest in the photochemistry of the stratospheric ozone layer. Data pertinent to this objective are obtained using balloon-borne instruments to measure the atmospheric transmission and emission in the mid infrared. In addition to obtaining constituent profile information, the spectral data obtained are also used to identify absorption or emission features which may interfere with the retrieval of constituent data from satellite instruments using lower spectral resolution.

SUMMARY OF PROGRESS AND RESULTS:

The primary instrumentation used on this program is a very high resolution (0.002 cm^{-1}) interferometer system. This system is interfaced with a solar tracking system so that high resolution solar spectra can be obtained while the unit is flown on a balloon. In order to enhance the sensitivity of the system to the detection and measurement of trace constituents the flights are performed so as to obtain data during solar occultation. The system has been flown three times during the period covered by this report. The first flight was performed from Ft. Sumner, New Mexico on November 18, 1987. The second flight was launched from Palestine, Texas on June 6, 1988 and the third flight was flown from Ft. Sumner, New Mexico on April 19, 1989. All three flights were complete successes and solar spectral data were obtained covering the region from 750 to 1925 cm^{-1} (5.2 to 13.3 microns) at solar zenith angles from 80° to 96° .

The spectral resolution obtained with the solar spectral system is 0.0025 cm^{-1} and represents about a factor of 5 greater resolution than any solar spectra previously obtained in this spectral region. As a result of the increase in spectral resolution a large number of features are observed in these spectra which were not observed in previous studies. Identification and analysis of these features is in progress. The results of this analysis to date shows a number of HNO_3 features which have not been observed before, and these occur where they will interfere with the retrieval of other constituents. An example of the interference is the occurrence of features in the 780.2 cm^{-1} region which overlap the ClONO_2 feature which will be used for retrieval of ClONO_2 by the CLAES instrument on UARS. A number of features due to COF_2 have also identified in the 1250 cm^{-1} region which may interfere with retrieval of N_2O_5 .

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In addition to the flights performed with the solar spectral instrumentation, a flight was also performed with an atmospheric emission radiometer system. The instrument was flown from Kiruna, Sweden on January 23, 1989 as part of the European Arctic campaign. For this flight, optical filters were chosen which were centered on the HNO_3 emission in the $11\mu\text{m}$ region. This flight was also a success, and an HNO_3 profile was obtained.

PUBLICATIONS:

- Goldman, A., F.J. Murcray, D.G. Murcray, J.J. Kusters, C.P. Rinsland, J.-M. Flaud, C. Camy-Peyret and A. Barbe, "Isotopic Abundances of Stratospheric Ozone from Balloon-Borne High Resolution Infrared Solar Spectra," J. Geophys. Res., 94, 8467-8473, 1989.
- Goldman, A., R.D. Blatherwick, J.J. Kusters, F.J. Murcray, J. Van Allen, F.H. Murcray and D.G. Murcray, "Atlas of Very High Resolution Stratospheric IR Absorption Spectra; Preliminary Edition," Department of Physics, University of Denver, November 1988.
- Goldman, A., F.J. Murcray, R.D. Blatherwick, J.J. Kusters, F.H. Murcray, D.G. Murcray and C.P. Rinsland, "New Spectral Features of Stratospheric Trace Gases Identified from High Resolution Infrared Balloon-borne and Laboratory Spectra," submitted to J. Geophys. Res., January 1989.
- F.J. Murcray, J.J. Kusters, R.D. Blatherwick, J. Olson and D.G. Murcray, "High Resolution Solar Spectrometer System for Measuring Atmospheric Constituents," submitted to Appl. Opt., March 1989.

A. RESEARCH TASK:

Thermal Emission Spectroscopy of the Middle Atmosphere

B. INVESTIGATORS AND INSTITUTIONS

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M.M. Abbas, Marshall Space Flight Center, Huntsville, AL 35812

C. RESEARCH OBJECTIVES

The general objective of this research is to obtain, via remote sensing, simultaneous measurements of the vertical distributions of stratospheric temperature, ozone, and trace constituents that participate in the catalytic destruction of ozone (NO_y : NO , NO_2 , NO_3 , HNO_3 , ClONO_2 , N_2O_5 , HNO_4 ; Cl_x : HOCl), and the source gases for the catalytic cycles (H_2O , CH_4 , N_2O , CF_2Cl_2 , CFCl_3 , CCl_4 , CH_3Cl , CHF_2Cl , etc.). Data are collected during a complete diurnal cycle in order to test our present understanding of ozone chemistry and its associated catalytic cycles. The instrumentation employed is an emission-mode, balloon-borne, liquid-nitrogen-cooled Michelson interferometer-spectrometer (SIRIS), covering the mid-infrared range with a spectral resolution of 0.020 cm^{-1} . Cryogenic cooling combined with the use of extrinsic silicon photoconductor detectors allows the detection of weak emission features of stratospheric gaseous species. Vertical distributions of these species are inferred from scans of the thermal emission of the limb in a sequence of elevation angles.

D. SUMMARY OF PROGRESS AND RESULTS

The fourth SIRIS balloon flight was carried out from Palestine, Texas on September 15-16, 1986 with 9 hours of nighttime data (40 km). High quality data, with spectral resolution 0.022 cm^{-1} , were obtained for numerous limb sequences. Fifteen stratospheric species have been identified to date from this flight: five species from the NO_y family (HNO_3 , NO_2 , NO , ClONO_2 , N_2O_5), plus CO_2 , O_3 , H_2O , N_2O , CH_4 , CCl_3F , CCl_2F_2 , CHF_2Cl , CF_4 , and CCl_4 . The nighttime values of N_2O_5 , ClONO_2 , and total odd nitrogen have been measured for the first time, and compared to model results. Analyses of the diurnal variation of N_2O_5 within the 1984 and 1986 data sets, and of the 1984 ClONO_2 measurements, were presented in the literature.

The demonstrated ability of SIRIS to measure all the major NO_y species, and therefore to determine the partitioning of the nitrogen family over a continuous diurnal cycle, is a powerful tool in the verification and improvement of photochemical modeling.

E. JOURNAL PUBLICATIONS

(1) J.C. Brasunas et al., "Balloon-borne cryogenic spectrometer for measurement of lower stratospheric trace constituents," Cryogenic Optical Systems and Instruments II, Ramsey K. Melugin (Ed.), Proc. SPIE 619, 80-88, 1986.

- (2) V.G. Kunde et al., "Infrared spectroscopy of the lower stratosphere with a balloon-borne cryogenic Fourier spectrometer," Applied Optics, 26, 595, 1987.
- (3) M.M. Abbas et al., "Simultaneous Measurement of Stratospheric O_3 , H_2O , CH_4 , and N_2O Profiles From Infrared Limb Thermal Emissions," J.G.R., 92, 8343, 1987.
- (4) S.T. Massie et al., "Atmospheric Infrared Emission of $ClONO_2$ Observed by a Balloon-Borne Fourier Spectrometer," J.G.R., 92, 14806, 1987.
- (5) W. Shaffer et al., "Retrieval of Constituent Mixing Ratios from Thermal Emission Spectra," Applied Optics, 27, 3482, 1988.
- (6) J.C. Brasunas et al., "Cryogenic Fourier spectrometer for measuring trace species in the lower stratosphere," Applied Optics, 27, 4964, 1988.
- (7) V.G. Kunde, et al., "Measurement of nighttime stratospheric N_2O_5 from infrared emission spectra," G.R.L., 15, 1177, 1988.
- (8) W.C. Maguire et al., "Infrared emission high spectral resolution atlas of the stratospheric limb," Applied Optics, 28, 1048, 1989.

Measurement of HO₂ and Other Trace Gases in the Stratosphere Using a High Resolution Far-Infrared Spectrometer at 28 km

Investigators and Institutions:

Wesley A. Traub, Kelly V. Chance, and David G. Johnson
Harvard-Smithsonian Center for Astrophysics, Cambridge, MA

Steven C. Wofsy

Center for Earth and Planetary Physics, Harvard University, Cambridge, MA

Abstract of Research Objectives:

This research aims to measure the stratospheric concentration profiles of a number of trace gases involved in ozone photochemistry, using a high resolution Fourier transform spectrometer, telescope, and stabilized pointing system (the FIRS-2 system) on a high altitude balloon platform. Spectra are obtained at 0.004 cm⁻¹ resolution in the far-infrared (70-220 cm⁻¹) and the mid-infrared (350-700 cm⁻¹), using the thermal emission of the atmosphere itself as the spectral source. The research includes balloon flights with multi-instrumented gondolas, with the objectives of increasing the number of simultaneously-measured, related species, and of providing cross-checks among different measurement techniques.

Summary of Progress and Results:

There have been three successful balloon flights of the FIRS-2 system, taking place in October 1987, May 1988, and May 1989. The latter two flights also included the Jet Propulsion Laboratory (JPL) FILOS instrument, which measures stratospheric OH and several other species, on the gondola. A flight is currently scheduled for September 1989 including FIRS-2, FILOS, and the JPL BMLS instrument (for measuring ClO) on the same gondola. The purpose of this flight is to obtain measurements simultaneous in time and space of ClO, HO₂, and HOCl, as a test of their close chemical relationship, in addition to our usual species measurements.

Atmospheric molecules detected to date in spectra from FIRS-2 balloon flights include OH, HO₂, H₂O (including minor isotopic species and vibrational hot bands), O(³P), O₂ (including minor isotopic species), O₃ (including minor isotopic species and vibrational hot bands), HCl, HF, HOCl, NO₂, N₂O, HNO₃ and CO₂.

We have used FIRS-2 balloon flight spectra to obtain the first measurement of stratospheric HOCl, including altitude profiles and their diurnal variation. We have made very accurate determinations of the altitude profile of HO₂, including nighttime measurements and upper limits.

Publications:

Measurement of Stratospheric HOCl: Concentration Profiles, Including Diurnal Variation, K. V. Chance, D. G. Johnson, and W. A. Traub, *Journal of Geophysical Research* 94, 11,059-11,069, 1989.

Ozone Measurements During the Balloon Intercomparison Campaign, D. Robbins, J. Waters, P. Zimmerman, R. Jarnot, J. Hardy, H. Pickett, S. Pollitt, W. Traub, K. Chance, N. Louisnard, W. Evans, and J. Kerr, *Journal of Atmospheric Chemistry*, in press, 1989.

Intercomparison of Measurements of Stratospheric Hydrogen Fluoride, W. G. Mankin, M. T. Coffey, K. V. Chance, W. A. Traub, B. Carli, A. Bonetti, I. G. Nolt, R. Zander, D. W. Johnson, G. Stokes, C. B. Farmer, and R. K. Seals, *Journal of Atmospheric Chemistry*, in press, 1989.

Intercomparison of Stratospheric Water Vapor Profiles Obtained During the Balloon Intercomparison Campaign, D. G. Murcray, A. Goldman, J. Kusters, R. Zander, W. Evans, N. Louisnard, C. Alamichel, M. Bangham, S. Pollitt, B. Carli, B. Dinelli, S. Piccioli, A. Volboni, W. A. Traub, and K. Chance, *Journal of Atmospheric Chemistry*, in press, 1989.

Balloon Intercomparison Campaign: Results of Remote Sensing Measurements of HCl, C. B. Farmer, B. Carli, A. Bonetti, M. Carlotti, B. M. Dinelli, H. Fast, N. Louisnard, C. Alamichel, W. Mankin, M. Coffey, I. G. Nolt, D. G. Murcray, A. Goldman, G. Stokes, D. Johnson, W. Traub, K. Chance, R. Zander, L. Delbouille, and G. Roland, *Journal of Atmospheric Chemistry*, in press, 1989.

Stratospheric Hydroperoxyl Measurements, W. A. Traub, D. G. Johnson, and K. V. Chance, submitted for publication.

A. Title of Research Task

N 9 2 - 1 4 5 0 3

Far Infrared Balloon-Based Limb Emission Measurements of HO_x Gases in the Middle Atmosphere

B. Investigators and Institutions

P.I.: Dr. James M. Russell III, NASA Langley Research Center
Co-I's: Dr. Bruno Carli, IROE, Firenze, Italy
Dr. Ira G. Nolt, NASA Langley Research Center
Dr. Susan Solomon, NOAA Aeronomy Laboratory

C. Abstract of Research Objectives

The aim of the measurements is to obtain vertical mixing profiles of hydrogen and halogen trace gases and to study the related processes of diurnal change, OH/HO₂ ratio, and HO_x total budget involved in stratospheric ozone. The species to be measured in the first planned 1990 flight of this new series include OH, H₂O₂, HO₂, HOCl, HBr, HCl, HF, H₂O, HDO, O₃, and isotopic O³.

D. Summary of Progress

The principal efforts of this cooperative international program with the Italian group under Dr. B. Carli have been: (1) the refurbishment and updating by the Istituto di Ricerca sulle Onde Elettromagnetiche (IROE), Italy, of the high-resolution Fourier transform spectrometer, (2) detector system construction by LaRC with the assistance of the University of Oregon and Queen Mary College, and (3) gondola engineering and flight planning with the JPL group of J. Riccio. Major improvements for the flight instrument include the incorporation of an improved pointing system, an input telescope for better vertical resolution, a linear motor mirror drive, improved spectral filters, and detector systems. In addition, a completely new flight electronics command and control system has been built in Italy based on the results of a cooperative system design effort with LaRC engineers. Thermal/vacuum testing of the flight instrument is scheduled for early 1990 at LaRC.

In addition, the analysis of past flight data and algorithm development has continued as a collaborative effort between LaRC and the Italian groups at Florence and Bologna. Recent analyses have been completed for the retrieval of the OH concentration profile and the first measurement of the HBr column concentration.

E. Publications

Carli, B. and J.H. Park, "Simultaneous Measurement of Minor Stratospheric Constituents with Emission Far-Infrared Spectroscopy," J. Geophys. Res., 93, 3851-3865, 1988.

Carli, B., M. Carlotti, B.M. Dinelli, F. Mencaraglia, and J.H. Park, "The Mixing Ratio of the Stratospheric Hydroxyl Radical from Far-Infrared Emission Experiments," J. Geophys. Res., (in press), 1989.

Park, J.H., B. Carli, and A. Barbis, "Stratospheric HBr Mixing Ratio Obtained from Far-Infrared Emission Spectra," Geophys. Res. Lett., (in press), 1989.

RESEARCH SUMMARY

A. Title: Measurement of the Solar UV Flux in the Stratosphere

B. Principal Investigator: James E. Mentall
NASA/Goddard Space Flight Center
Greenbelt, MD 20771
(301) 286-8959

C. Abstract:

Measurements of the direct solar flux from balloons at an altitude of 40 km are used to determine the effective cross sections of the Schumann-Runge bands. Transmission in these bands, which lie between 180 and 200 nm, allows the Sun's radiation in this region of the spectrum to penetrate into the lower mesosphere. Measurements by a high resolution scanning spectrometer (0.02 nm) is used to measure the transmission in the Schumann-Runge bands. Since ozone also absorbs in this wavelength region, a low resolution scanning spectrometer (0.25 nm) measures the transmission between 220 and 260 nm allowing the column ozone to be determined. Absorption due to Ozone can then be calculated and the data corrected for this effect.

D. Summary of Progress and Results:

After several failures of the solar pointing system, a successful flight has been obtained. Data from this flight is being analyzed.

Biennial Research Summary

A. Title: Stratospheric Fourier Spectroscopy

B. Principal Investigator: Geoffrey C. Toon
MS 183-401
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena CA 91109

C. Abstract of Research Objectives:

To measure high resolution infrared solar absorption spectra from ground-based, airborne and balloon-borne platforms using the JPL MkIV interferometer. These spectra will then be analyzed in order to determine the abundances of 20-30 different atmospheric gases, many of which play a central role in determining the global distribution of ozone. These spectra will be measured in a variety of latitudes and seasons in order to test photochemical models of the atmospheric composition under a range of different conditions.

D. Summary of Progress and Results during 1988 and 1989:

The main activity during the first part of 1988 was the analysis of some 1000 spectra recorded from the DC-8 aircraft during the AAOE campaign of 1987. This work confirmed our findings of the NOZE I campaign of 1986: the interior of the vortex is depleted in NO₂, HNO₃ and HCl; large quantities of ClNO₃ reside at the vortex edge; and descent occurs within the vortex, as implied by the depleted abundances of tropospheric source gases such as N₂O, CH₄, CFC-12, together with enhanced abundances of HF.

During the second half of 1988 preparation were made for the 1989 AASE campaign. This included installation of the MkIV interferometer back onto the NASA DC-8 aircraft at the NASA Ames facility followed by three test flights. To perform rapid analysis of the our spectra in the field a new computer system was purchased and processing and analysis software was developed on this system.

During the first six weeks of 1989 the MkIV interferometer team were in Stavanger, Norway, participating in the AASE campaign. Over the course of more than a dozen DC-8 flights, more than 2000 spectra (4 Gbytes of data) were recorded. We were able to coarsely analyze the spectra for O₃, NO, NO₂, HNO₃, HCl, ClNO₃ and H₂O within 24 hours of each DC-8 flight, allowing these results to be factored into the planning of subsequent flights. The results themselves show an unexpected similarity to those obtained over Antarctica, with the exception that the abundances of HNO₃ and H₂O were much larger in the North, a consequence of the warmer temperatures.

Since the AASE campaign, our main thrust has been in the preparation for the Fall 89 balloon flight from Fort Sumner, New Mexico. Although this will its first balloon flight, it must not be forgotten that the MkIV interferometer was originally designed to fly on balloons and that limb sounding from a platform at 40km altitude is undoubtedly the optimum geometry for investigating the composition of the stratosphere. We therefore anticipate some exciting results from this flight.

E. Journal Publications in 1988 & 1989

G.C.Toon, C.B.Farmer, P.W.Schaper, J.-F.Blavier and L.L.Lowes
"Ground-based infrared measurements of tropospheric source gases over Antarctica during the 1986 Austral Spring", JGR (in press)

G.C.Toon, C.B.Farmer, L.L.Lowes, P.W.Schaper, J.-F.Blavier and R.H.Norton, "Infrared Aircraft measurements of stratospheric composition over Antarctica during September 1987" JGR (in press)

G.C.Toon and C.B.Farmer, "Detection of HOCl in the Antarctic Stratosphere", accepted by GRL

S.Kinne, O.B.Toon, G.C.Toon, C.B.Farmer, E.V.Browell and M.P.McCormick, "Measurements of size and composition of particles in polar stratospheric clouds from solar absorption spectra", JGR (in press)

J.J.Margitan, G.A.Brothers, E.V.Browell, D.Cariolle, M.T.Coffey, J.C.Farmen, C.B.Farmer, G.L.Gregory, J.W.Harder, D.J.Hoffman, W.Hypes, S.Ismail, R.O.Jakoubek, W.Komhyr, S.Kooi, A.J.Krueger, J.C.Larsen, W.Mankin, M.P.McCormick, G.H.Mount, M.H.Proffitt, A.R.Ravishankara, A.L.Schmeltekopf, W.L.Starr, G.C.Toon, A.Torres, A.F.Tuck, A.Wahner, I.Watterson, "Intercomparison of ozone measurements over Antarctica", JGR (in press)

A. Title of Research Task: Balloon Microwave Limb Sounder (BMLS) stratospheric measurements.

B. Investigators: R.A. Stachnik and J.W. Waters
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

C. Abstract of Research Objectives: The objective of this program is measure abundance and variability of stratospheric trace constituents which influence stratospheric ozone using balloon-borne millimeter and sub-millimeter wave spectrometers. The present instrumentation simultaneously measures O_3 and ClO , a key indicator of Cl -catalyzed O_3 destruction. A second instrument, now being built, will have a capability to simultaneously measure ClO , O_3 , HCl , HO_2 , HNO_3 , and N_2O . This program also provides a background for development of satellite instrumentation which can yield measurements on a global scale. Technology developed by this program has been used in the Microwave Limb Sounder (MLS) instrument on Upper Atmosphere Research Satellite (UARS) and will be essential to the development of the proposed MLS instrument on the Earth Observing System (EOS) platform.

D. Summary of Progress and Results:

1. The BMLS instrument was successfully flown from the National Scientific Balloon Facility (NSBF) site at Ft. Sumner NM. in September 1988 and from the Palestine, TX site in May 1989. The latter flight was the first balloon-based measurement using the UARS MLS development filter bank spectrometers and provided measurements of both O_3 and ClO with approximately 15 minutes time resolution through a sunset transition. Representative raw spectral data from this flight for ClO is shown in Figure 1. Figure 2 shows retrieved ClO mixing ratio profiles from *single* limb scans. The BMLS instrument currently has spectral

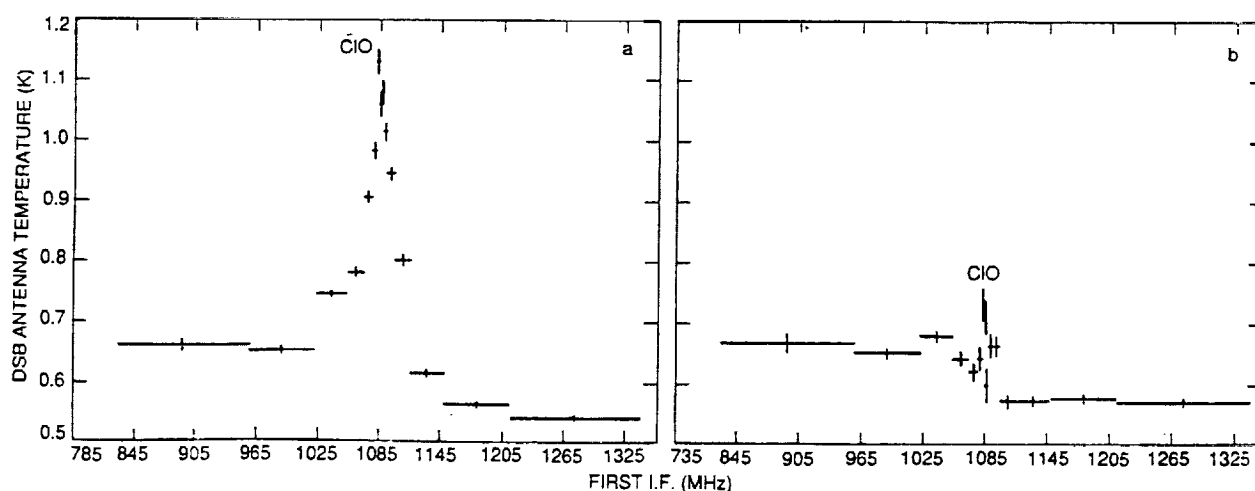


Figure 1: (a) Daytime ClO emission spectrum from 33-34 km tangent height. (b) Night ClO emission from 33-34 km. Integration time of each spectrum ~ 300 seconds.

coverage and resolution identical to that of the 205 GHz subsystem of the UARS MLS instrument. Publications of these results are in preparation.

2. Ground-based microwave measurements of stratospheric O_3 were made at the Jet Propulsion Laboratory Table Mountain Observatory in February-March 1989. These results were compared with simultaneous measurements by the JPL Table Mountain LIDAR and found to agree to within 5%.
3. A submillimeter wave radiometer is being built to provide simultaneous measurement of ClO , O_3 , HCl , HO_2 , HNO_3 , and N_2O and will be capable of balloon-borne or aircraft operation. The first balloon flight of this instrument is planned for September 1990.
4. A joint balloon flight of the BMLS instrument, the far infrared spectrometer of the Smithsonian Astrophysical Observatory, and the JPL far infrared limb observer is planned for September 1989 from Ft. Sumner NM. A goal of this effort is to determine the stratospheric abundance of chlorine as ClO , HCl and $HOCl$.

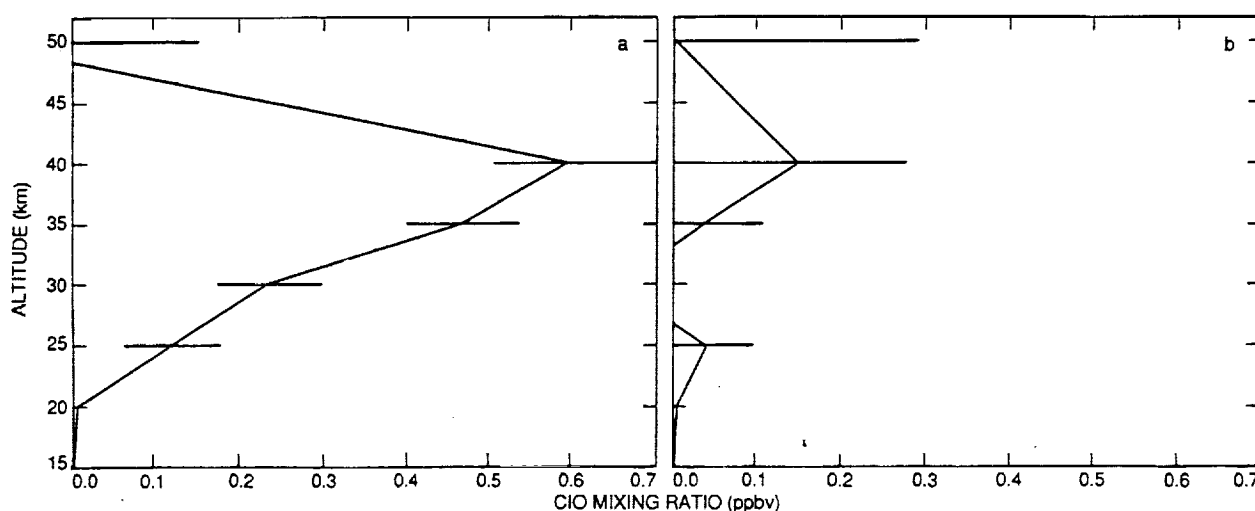


Figure 2: Retrieved ClO vertical profiles from *single* limb scans. Effective integration time is ~ 400 seconds for each profile. Profile times are: (a) 1245–1300 CDT 27 May 1989, and (b) 0200–0215 CDT 28 May 1989.

E. Journal Publications:

Waters, J.W., R.A. Stachnik, J.C. Hardy, R.F. Jarnot, "ClO and O_3 Stratospheric Profiles: Balloon Microwave Measurements", *Geophys. Res. Lett.*, 15, 780–783, 1988.

Robbins, D., J. Waters, P. Zimmermann, R. Jarnot, J. Hardy, H. Pickett, S. Pollitt, W. Traub, K. Chance, N. Louisnard, W. Evans, and J. Kerr, "Ozone Measurements from the Balloon Intercomparison Campaign", *J. Atmos. Chem.*, in press, 1989.

A. Stratospheric Constituent Distributions From Balloon-Based Limb Thermal Emission Measurements

B. Mian M. Abbas
Space Science Laboratory
NASA Marshall Space Flight Center
Huntsville, Al 35812

and

Vigil G. Kunde
Laboratory for Extraterrestrial Physics
NASA Goddard Space Flight Center
Greenbelt, MD 20771

C. Research Objectives

This research task deals with an analysis of infrared thermal emission observations of the earth's atmosphere for determination of trace constituent distributions. Infrared limb thermal emission spectra in the 700–2000 cm^{-1} region were obtained with a liquid nitrogen cooled Michelson interferometer–spectrometer (SIRIS) on a balloon flight launched from Palestine, Texas, at nighttime on September 15–16, 1986. An important objective of this work is to obtain simultaneously measured vertical mixing ratio profiles of O_3 , H_2O , N_2O , NO_2 , N_2O_5 , HNO_3 and ClONO_2 and compare with measurements made with a variety of techniques by other groups as well as with photochemical model calculations.

C. Summary of Progress and Results

A portion of the observed spectra obtained by SIRIS from the balloon flight on September 15–16, 1986, has been analyzed with a focus on calculation of the total nighttime odd nitrogen budget from the simultaneously measured profiles of important members of the NO_x family. The molecular spectral data employed in the calculations is based on the AFGL compilation HITRAN, 1986 (Rothman et al., 1987). The ClONO_2 parameters are taken from the database of Rinsland et al., (1985) employing laboratory crosssections of Massie et al., (1985) with normalization to measurements by Graham et al. (1977). For N_2O_5 , room temperature absorption coefficients based on laboratory transmittance measurements of Massie et al. were used. The temperature profile used in the analysis was obtained from the soundings made by National Meteorological Center near the balloon track.

The measurements permit first direct determination of the nighttime total odd nitrogen concentrations NO_y and the partitioning of the important elements of the NO_x family. The total odd nitrogen concentration $[\text{NO}_y]$ is defined here as $[\text{NO}_y] = [\text{NO}] + [\text{NO}_2] + [\text{NO}_3] + [\text{N}_2\text{O}_5] + [\text{HNO}_3] + [\text{HNO}_4] + [\text{ClONO}_2]$. NO is quickly converted into NO_2 at night and its contribution to the total odd N nighttime budget can be ignored. The distributions of NO_3 and HNO_4 have not been made in the present set of measurements by SIRIS. In calculation of the total odd nitrogen budget, predicted profiles based on a 1-d photochemical model have been employed for both of these constituents. Comparisons of the total odd nitrogen budget are made with the daytime measurements by the ATMOS experiment, and with the predictions of the 1-d and 2-d photochemical models.

E. Publications

(1) "Measurement of nighttime stratospheric N_2O_5 from infrared emission spectra", V. G. Kunde, J. C. Brasunas, W. C. Maguire, J. R. Herman, S. T. Massie, M. M. Abbas, L. W. Herath, and W. A. Shaffer, *Geophys. Res. Lett.*, 15(11), 1177–1180, 1988.

(2) "Nighttime measurements of stratospheric NO_x from balloon-borne limb thermal emission observations," M. M. Abbas, V. G. Kunde, J. C. Brasunas, W. C. Maguire, J. R. Herman, S. T. Massie, and W. A. Shaffer, *Proc. Quadrennial Ozone Symposium* (held Gottingen, Federal Republic of Germany, August 8–13, 1988).

(3) "High resolution balloon-borne emission spectroscopy of trace species in the lower stratosphere: N_2O_5 , HNO_3 ," *ibid.*

Title: Far Infrared Balloon Radiometer for OH

Investigators: Herbert M. Pickett and Dean B. Peterson
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

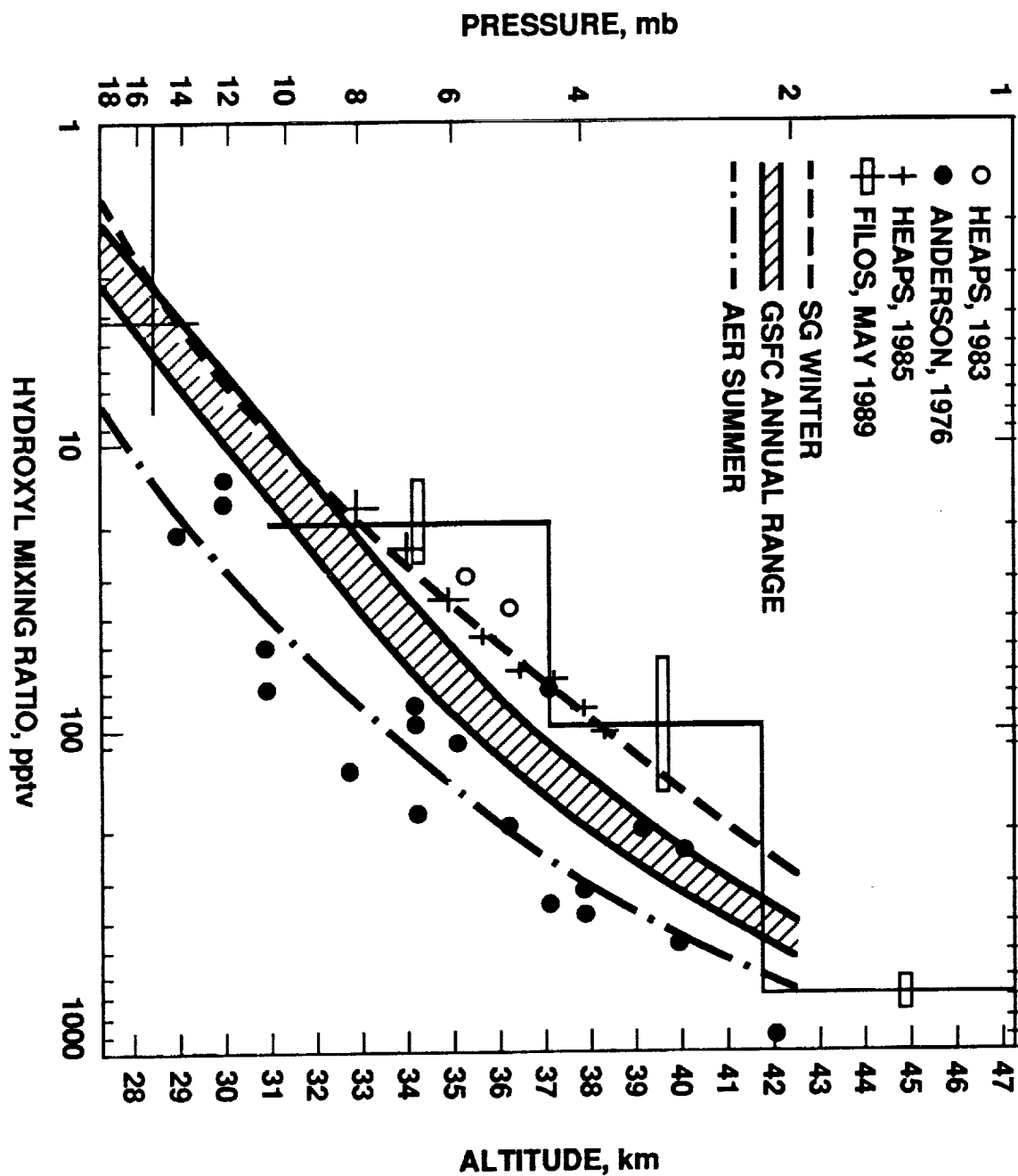
Objectives: A stratospheric hydroxyl radical (OH) radiometer for balloon observations in the far infrared region of the spectrum is being developed. The instrument uses three Fabry-Perot resonators to resolve stratospheric limb emission of OH at 101 cm^{-1} ($99\text{ }\mu\text{m}$ wavelength). The spectral resolution of 0.001 cm^{-1} is used to match the width of the stratospheric OH emission. The instrument is compact and designed to fly jointly with other balloon measurements. The goal of this task is to determine OH concentrations from 25-45 km with better than 10% accuracy.

Progress and Results: The first scientific balloon flight was made on May 15, 1989. OH radical emission from two different lines was definitely identified during the day and decayed as expected after sunset. Features due to HDO, vibrationally excited H_2O , and O_3 were also identified. Provisional retrievals of the OH have shown that the OH is consistent with models for OH concentration within experimental error. In September, this instrument will fly from Ft. Sumner, NM, jointly with the Microwave Limb Sounder and with the Harvard Smithsonian Astrophysical Observatory Far Infrared Spectrometer. These joint measurements will allow comparison of OH and O_3 determinations.

During the year, significant improvements in Fabry-Perot resonator performance have been made, including better flatness and more predictable performance with cooling to 4K. Test capability has been greatly enhanced through use of a high resolution FTS instrument for filter positioning and through use of a HeNe laser based Fizeau interferometer. The end-to-end performance of the instrument in the laboratory has been verified by measuring a HDO sample in emission against a liquid N_2 black-body. This signal is close to the atmospheric OH signal and comparable in emission strength.

Publications: Publications on the instrument design and OH results will be prepared in the coming year.

HYDROXYL PROFILE



MULTI-SENSOR BALLOON MEASUREMENTS

147-16-01-40

J. H. Riccio, Jet Propulsion Laboratory

OBJECTIVES

Continuing technical, logistical, and operational support of stratospheric balloon flights is conducted to measure the abundance and altitude distribution of key chemical constituents in the upper atmosphere. Two modular gondola systems are available to carry multi-instrument packages, consisting of several JPL remote sensing instruments and instruments from other institutions in the U. S. and abroad. The payloads are configured for a particular scientific objective. Data are obtained on the altitude profiles for a number of chemically coupled species from one or more flights in the same air mass and at the same time for the purposes of instrument intercomparison, testing of atmospheric chemical models, and validation of satellite data.

SUMMARY OF PROGRESS AND RESULTS

The past two years have seen a marked increase in the rate of stratospheric balloon flights. In the Spring of 1988 the BLISS instrument (JPL, Webster P. I.) was launched successfully from the NSBF facility at Palestine, TX. In the fall of 1988 the BLISS and OZONE (JPL, Margitan, P. I.) instruments were successfully flown from Palestine, TX, and the BMLS (JPL, Stachnik, Waters, co-P. I.s) instrument was successfully flown from the Ft. Sumner, N. M. facility. In Spring of 1989 four instruments were launched at Palestine, including OZONE, BMLS, FILOS (JPL, Pickett, P. I.), and FIRS-2 (SAO, Traub, Chance, co-P. I.s). Fall of 1989 saw the launch at Ft. Sumner of a multi-instrument gondola carrying FIRS-2, FILOS, and BMLS, all of which operated successfully. Shortly afterward, MARK-IV (JPL, Toon, P. I.) was launched with the OZONE instrument, again from Ft. Sumner.

C. GROUND-BASED MEASUREMENTS

TITLE OF RESEARCH TASK: Collecting, Analyzing and Archiving of Ground Based Infrared Solar Spectra Obtained from Several Locations.

INVESTIGATORS: David G. Murcray, Physics Department, University of Denver
 Frank J. Murcray, Physics Department, University of Denver
 Aaron Goldman, Physics Department, University of Denver
 Charles T. McElroy, Physics Department, University of Denver
 William P. Chu, NASA Langley Research Center
 Curtis P. Rinsland, NASA Langley Research Center
 Peter Woods, National Physical Laboratory, England
 W.A. Matthews, Dept. of Sci. and Indust. Res., New Zealand
 P.V. Johnston, Dept. of Sci. and Indust. Res., New Zealand

ABSTRACT OF RESEARCH OBJECTIVES:

The infrared solar spectrum as observed from the ground under high resolution contains thousands of absorption lines. The majority of these lines are due to compounds that are present in the Earth's atmosphere. Ground based infrared solar spectra therefore contain information concerning the composition of the atmosphere at the time the spectra were obtained. The objective of this program is to record solar spectra from various ground locations, and to analyze and archive these spectra. The analysis consists of determining, for as many of the absorption lines as possible, the molecular species responsible for the absorption, and to verify that current models of infrared transmission match the observed spectra. Archiving is an important part of the program since a number of the features in the spectra have not been identified. At some later time, when the features are identified, it will be possible to determine the amount of that compound that was present in the atmosphere at the time the spectrum was taken.

SUMMARY OF PROGRESS AND RESULTS:

Our high resolution ($.01 \text{ cm}^{-1}$) interferometer system was used during NOZE-2 (Sept. and Oct. 1987) to measure HNO_3 , HCl and other stratospheric gases from McMurdo, Antarctica. It was operated again in the austral spring of 1988 and 1989 in cooperation with investigators from the New Zealand DSIR. Results from the first two years are very similar, with variable HNO_3 , and a steady increase in HCl from a very low value.

On its way to and from Antarctica, the instrument has been set up and operated from the DSIR station at Lauder, New Zealand. Observing periods there include August 1988, Dec. 1988 and Jan. 1989, and August 1989. The set of HNO_3 observations from Lauder extends back to 1985, and indicates either a significant annual cycle, a significant long-term increase, or both.

Much of the work with our very high resolution ($.002 \text{ cm}^{-1}$) system has been directed toward development of instrumentation for the Network for the

Detection of Stratospheric Change. We have operated the instrument on the ground for several days in preparation for balloon flights, and those data are being analyzed and stored for the development of retrieval algorithms for the Network.

PUBLICATIONS:

Murcray, F.J., F.H. Murcray and D.G. Murcray, "Infrared Measurements of Abundances of Several Trace Gases in the Antarctic Atmosphere," Rev. of Geophys., 26, 81-88, 1988.

Matthews, W.A., P.V. Johnston, D.G. Murcray, F.J. Murcray and R.D. Blatherwick, "Column Abundance of Hydrogen Chloride above Lauder, New Zealand," in press, 1988.

Rinsland, C.P., A. Goldman, F.J. Murcray, F.H. Murcray and D.G. Murcray, "Infrared Measurements of Atmospheric Gases above Mauna Loa, Hawaii in February 1987," J. Geophys. Res., 93, 12607-12626, 1988.

Murcray, F.J., W.A. Matthews, A. Goldman, P.V. Johnston and C.P. Rinsland, "HN₃ Column Abundance over Lauder, New Zealand," J. Geophys. Res., 94, 2235-2238, 1989.

MEASUREMENT OF STRATOSPHERIC CHLORINE MONOXIDE AND OTHER TRACECONSTITUENTS FROM A PORTABLE GROUND-BASED MM-WAVE SYSTEM

Robert de Zafra and Philip M. Solomon, Co-principal Investigators
State University of New York, Stony Brook, N.Y. 11794

Research Objectives:

- A.) To reduce, analyze, and prepare for publication the results of field observations conducted during September and October, 1987, at McMurdo Station, Antarctica;
- B.) To continue the measuring and monitoring of ClO in the stratosphere over Mauna Kea, Hawaii (20 N latitude), with particular attention to the determination of long term changes (years to decade time span) and to improve the measurement of its diurnal variation;
- C.) To measure O₃, N₂O, and HCN with emphasis on vertical profile recovery and short-term (e.g., seasonal) variations, related to variability in transport and production.

Summary of Progress and Results:

Data Analysis of Antarctic Field Observations: This work consumed considerable time during 1988 and led to three papers discussing our findings. Despite generally much poorer (weather-related) observing conditions at McMurdo during the fall of 1987, a good block of data was obtained, with twice the spectral bandwidth used for our initial discovery of anomalous low-altitude Antarctic ClO in 1986. This new data, with its greater spectral coverage, allowed a reasonably accurate profile recovery to be made for the mixing ratio of ClO down to about 17 km, and also the determination of the altitude (19.5 ± 1 km) at which the mixing ratio reached its maximum value (1.6 ± 0.4 ppb), as well as a good measure of diurnal variation of the low-altitude ClO layer found in Antarctica during the period of seasonal ozone depletion.

This data (de Zafra, et al., 1989) provides a substantial improvement over our profile determinations from 1986 data, but served to confirm and strengthen, rather than alter, the conclusions reached from the previous year's discovery. The present data, with a reasonably detailed measurement of the ClO mixing ratio as a function of altitude over the stratospheric layer in which ozone is being destroyed, allowed us to evaluate the rate at which the ClO dimer formation mechanism can act to return free chlorine to continue the catalytic ozone destruction cycle. The probability of ClO dimer formation depends upon the product of background air pressure and the square of ClO concentration, and thus varies very strongly over the altitude range in which the low-level ClO exists. From this analysis, an estimate of the rate of ozone destruction can be made as a function of altitude. We compared this rate with the observed rate of ozone loss at various altitudes as measured by direct balloon sounding, and found very good agreement (Barrett, et al., 1988), suggesting that the dimer mechanism is capable of closing the chlorine-ozone catalysis cycle with an efficiency high enough to explain the rapid loss of ozone now being observed.

We have also analyzed measurements of HCN taken at McMurdo in both 1986 and 1987, and shown that these tend to indicate that a substantial subsidence of stratospheric air has occurred over Antarctica by the end of the winter period, as previously indicated by our measurements of anomalously small amounts of the 'stable' tracer N₂O in 1986. A complicating factor in the case of HCN arises from evidence that the tropical or mid-latitude profile of this species is not in agreement with current theory (Jaramillo, et al., 1989), so that our analysis had to be based on a comparison of Antarctic with tropical

measurements, and does not take into account chemical or photo-processing which may modify the HCL profile during transport from low-latitude sources to Antarctica.

At the end of the summer (1988) the equipment was returned to Mauna Kea for the first time since June 1986, after it was checked and minor repairs were made at Stony Brook. Partly as a result of poor weather and partly because of technical problems and a short time allocated for this trial run, no good-quality emission data was collected. A second run was carried out in November 1988, with the intention of carefully analyzing and improving some questionable performance noted in the first run. Again the weather was unusually poor (frequent storms, nearly continuous high humidity), but considerable progress was made in improving the equipment performance, and some useful data was taken on N_2O and HNO_3 during one moderately good break in the weather.

A significant modification was made on part of the equipment at Stony Brook during the early spring, to improve the broad-band baseline flatness, and a third run was made in late May-early June, 1989. A substantial improvement in baseline flatness over the full 512 MHz passband of the present equipment was noted. Again the weather was uncooperative, and only N_2O data was obtained. (The entire period from the late summer of 1988 through the late spring of 1989 was one of unusually frequent storms, cloud overcast, and unusually high humidity at Mauna Kea - the worst period in our experience. Much of the astronomical program at the observatory was crippled, as well as our own work. There is some belief that this problem is associated with a current "anti-El Nino" cycle in the Pacific, and should soon end.)

Journal Publications During This Period.

"Formation of the Antarctic Ozone Hole by the ClO Dimer Mechanism", J.W. Barrett, P.M. Solomon, R.L. de Zafra, M. Jaramillo, L.Emmons, and A.Parrish, Nature, 336, 455-458, 1988.

"mm-Wave Observations of Stratospheric HCN at Tropical Latitudes." M.Jaramillo, R.L.de Zafra, J.W.Barrett, A.Parrish, and P.M.Solomon, Geophys. Res. Letters, 15, 265-268, 1988.

"Observation of Extremely Low N_2O Concentrations in the Springtime Stratosphere at McMurdo Station, Antarctica." A. Parrish, R.L. de Zafra, M. Jaramillo, B. Connor, P.M. Solomon, and J.W. Barrett, Nature, 332, 53-55, 1988.

"New Observations of a Large Concentration of ClO in the Springtime Lower Stratosphere over Antarctica and its Implications for Ozone-Depleting Chemistry", R.L. de Zafra, M.Jaramillo, J.Barrett, L.K. Emmons, P.M. Solomon, and A. Parrish, to be published in J. Geophys. Res.(special issue), 1989

"Measurements of Stratospheric Hydrogen Cyanide at McMurdo Station, Antarctica: Further Evidence of Winter Stratospheric Subsidence?", M. Jaramillo, R.L. de Zafra, J. Barrett, L.K. Emmons, P.M. Solomon, and A. Parrish, to be published in J. Geophys. Res. (special issue), 1989.

A. Title of Research Project: Global Atmospheric Gases Experiment: Calibration, Oregon Station and Samoa Station

B. Investigators: R.A.Rasmussen & M.A.K.Khalil, Institute of Atmospheric Sciences, Oregon Graduate Center, Beaverton, Oregon 97006, U.S.A.

C. Research Objectives: The research had 6 objectives:

- (1) To continue systematic, in-situ, high precision measurements of F-11, F-12, CH₃CCl₃, CCl₄, N₂O, CH₄ and F-113 at Samoa and Oregon stations (similar experiments were done at Barbados and Tasmania by other members of the GAGE team).
- (2) Improving the calibration standards to ensure the long-term stability and accuracy for measuring the halocarbons, CH₄ and N₂O.
- (3) Use flask samples to corroborate the real-time measurements.
- (4) Maintain and increase the air stored for future analyses (air bank) of new species.
- (5) Collate, manage and enter the data on our computer systems and prepare it for analysis.
- (6) Analyze the data for trends, lifetimes and mass balances of the gases measured.

D. Findings (1988-1989):

During 1988-1989, concentrations of F-11, F-12, F-113, CHCl₃, CH₃CCl₃, CCl₄, N₂O and CH₄ were measured at Samoa and Oregon and are now a part of the long-term GAGE data base. The other tasks listed above were also successfully completed.

For more than a decade, we have taken systematic, in situ, global measurements of F-11, F-12, N₂O, CCl₄, and CH₃CCl₃ as an integral part of the Atmospheric Lifetime Experiment (ALE) and for the Global Atmospheric Gases Experiment (GAGE) using automated instruments. Recently continuous measurements of CH₄ and F-113 were also added. During the last year we have evaluated the usefulness of such intensive automated measurements compared to collection of air in flask samples that are sent to our laboratory for detailed analysis. We have concluded that the automated sampling and analysis used in the ALE/GAGE program has substantial benefits if confined to 1-3 years to establish the climatology of these long-lived gases. After that time the process of continuous monitoring brings diminishing returns and is inferior to regular flask sampling.

In summary, the benefits of flask sampling compared to continuous monitoring are:

- (1) It is practical to increase sampling frequency for short periods to equal that of continuous monitoring. Any information requiring intensive measurements can be obtained also by flask sampling schedules.
- (2) Many more trace gases can be measured simultaneously instead

of just a few with continuous monitoring. In particular there are a number of environmentally important trace gases for which continuous automated measurements are not yet possible or practical. These include non-methane hydrocarbons, F-22 and man-made bromine containing gases such as CF₃Br and CF₂BrCl and the CFC replacements compounds HCFC-123 and HCFC-134a.

(3) The overall costs of measurements by flask sampling are only a small fraction of the costs of continuous monitoring.

(4) Flask samples provide an opportunity to verify measurements that appear unusual.

(5) Flask samples provide a means to archive air for future analyses and verification of data and absolute calibration.

(6) Most importantly, with flask sampling, stable primary laboratory calibration standards can be maintained for decades. There are proven methods to make and keep stable calibration standards for a decade or more. For continuous field measurements many secondary calibration standards have to be prepared and used over the years. The ALE-GAGE program has consumed over 300 secondary standards. These secondary standards, no matter how carefully prepared, introduce uncertainties that grow in time causing the long-term data to be less reliable than flask sampling data based on a single or several primary standards. In the ALE/GAGE program the flask samples were often used to correct the absolute concentrations as the continuous measurements drifted or were affected by variations of secondary standards.

(7) Over the years we have maintained an independent flask sampling network that has produced all the results obtained from the ALE/GAGE program and have established the importance and usefulness of flask sampling techniques. Many results from the network have been published. In some cases the work based on flask samples has turned out to be more reliable than from continuous monitoring. In general we have found that weekly flask samples provide the same information on trends and lifetimes of the trace gases measured in the ALE/GAGE program as the continuous measurements.

At present we are using the data obtained from the ALE/GAGE program to arrive at the best flask sampling strategies for long-term measurements of long-lived and moderate-lived trace gases.

E: Journal Publications (1988-1989):

"Global Distribution of Trace Organo-Bromine Gases," Ph.D. Dissertation, Rohith Gunawardena, 1989, Oregon Graduate Center.

"Ozone Destruction and Photochemical Reactions at Polar Sunrise in the Lower Arctic Atmosphere," L.A. Barrie, J.W. Bottenheim, R.C. Schnell, P.J. Crutzen, and R.A. Rasmussen. Nature 334, 138-141, 1988.

"The Role of Methylchloroform in the Chlorine Budget," M.A.K. Khalil and R.A. Rasmussen. Paper 89-5.4, AWMA 82nd Annual Meeting, June 1989, Anaheim, California.

- A. Latitudinal Gradients in Tropospheric Concentrations of Selected Halocarbons and Hydrocarbons (NAGW-452)
- B. Professor F. Sherwood Rowland, Department of Chemistry, University of California, Irvine, California, 92717
- C. The primary goal of this project is the understanding of the global sources, sinks, and distribution of volatile gaseous trace species. The basic experimental input for these studies is the measurement of the atmospheric mixing ratios of numerous halocarbons (CFCs, especially CCl_3F , CCl_2F_2 , and $\text{CCl}_2\text{FCClF}_2$; CH_3CCl_3 , CCl_4 , $\text{CCl}_2\text{-CCl}_2$, and others), hydrocarbons (CH_4 , alkanes to C_6H_{14} , C_2H_2 , several olefins), and carbon monoxide every three months on a regular grid from 71°N (Barrow, Alaska) to 47°S (New Zealand). The air samples are collected at ground level in remote locations, away from sources of these compounds, and then returned to the home laboratory for analysis by gas chromatography. The measurements provide information about the growth in atmospheric mixing ratios of the longer lived species (e.g. CH_4 , CFCs, CCl_4 , CH_3CCl_3). They also demonstrate the pronounced seasonal and latitudinal mixing ratio differences found for molecules such as CO , CC_2H_6 , and C_3H_8 which have atmospheric lifetimes of less than a year. Correlation among the mixing ratios of different compounds provide details about source and sink relationships. Global average mixing ratios are calculated for the longer-lived molecules from the average concentrations in 16 equal area latitudinal bands.
- D. Our measurements of the average global mixing ratios of methane have shown a monotonic increase from 1.52 ppmv in January 1978 to 1.70 ppmv in June 1989, for an average yearly increase of 16 ppbv over 11.5 years. The best fit to this data series indicates a gradual slowing in the yearly rate of increase in methane concentrations, but the non-linearity is not large and is only marginally significant statistically. No substantial deviations for isolated geophysical events (e.g. eruption of El Chichon volcano) have been found, with a one-sigma standard error of only 0.003 ppmv for deviation from a linear fit for 27 data periods over 11.5 years.

Our data for $\text{CCl}_2\text{FCClF}_2$ (CFC-113) continue to display a rapidly increasing atmospheric mixing ratio, having risen from about 15 pptv in the northern hemisphere in 1977 to about 75 pptv in mid-1989. The tonnage of $\text{CCl}_2\text{FCClF}_2$ emitted to the atmosphere yearly is almost as large as for CCl_3F (CFC-11). Urban air samples in major U.S. and Japanese cities often exhibit $\text{CCl}_2\text{FCClF}_2$ as the most prominent halocarbon added by local emission, although 28 more halocarbons with no more than two carbon atoms have been readily identified in our analyses.

The strong seasonal variation in C_2H_6 mixing ratios continues, consistent with a source almost entirely in the northern hemisphere land masses and reaction with hydroxyl radical as the only major sink. The seasonal variation for C_2H_6 is about a factor of 2.5 in each hemisphere, with maximum mixing ratios in the winter. The northern winter concentrations are in the 2 to 3 ppbv range, while the southern summer values generally fall between 0.1 and 0.2 ppbv. Although not yet measured on a global basis, hydroxyl radical concentrations are much lower in the larger winter solar with zenith angles and colder temperatures, allowing the build-up of C_2H_6 mixing ratios. On the basis of more than 3 years of CO measurements, the northern hemispheric mixing ratios peak at

about 150 ppbv in temperate latitudes, and drop to 80 ppbv in the summer. The southern hemispheric seasonal variations are less, ranging only between about 40 and 55 ppbv. The mixing ratios of CO in the southern hemisphere are consistent with the oxidation of CH₄ by HO as the predominant carbon source. Because the CH₄ north/south mixing ratio is only about 1.1, the major source of the much more abundant northern hemisphere CO is not CH₄, but a combination of direct CO emission and atmospheric oxidation of various non-methane hydrocarbons (NMHC).

Our current detailed analyses have been extended to enough rapidly-reacting molecules that large mixing ratio variations are often encountered, and occasional data are indicative of a major source in close proximity to the location of the air sampling, e.g. isoprene in the vicinity of the jungles of the Solomon Islands.

- E. Blake, D. R., and F. S. Rowland, World-wide increase in tropospheric methane, 1978 to 1987, *Science*, 239, 1129-1131, 1988.
- Rowland, F. S., Chlorine chemistry in the antarctic stratosphere, *Preparing for Climate Change, Proceedings of the First North American Conference of Preparing for Climate Change*, October 27-29, 1987, Washington, DC, Government Institutes, Inc., 55-76, 1988.
- Rowland, F. S., Some aspects of chemistry in the springtime antarctic stratosphere, *The Changing Atmosphere*, John Wiley & Sons, Chichester, United Kingdom, 121-140, 1988.
- Rowland, F. S., Chlorofluorocarbons, stratospheric ozone and the antarctic ozone hole, *Environmental Conservation*, 15, 101-115, 1988.
- Rowland, F. S., The role of halocarbons in stratospheric ozone depletion, *Ozone Depletion, Greenhouse Gases, and Climate Change*, National Academy Press, Washington, DC, 1989.
- Rowland, F. S., Chlorofluorocarbons and stratospheric ozone depletion, *American Scientist*, 77, 36-45, 1989.

A. Ground-based Observations and Theoretical Studies of the Vertical Column
Abundance of Atmospheric Hydroxyl

B. Co-investigators:

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Supported by NASA (NAGW-989), NSF, & NOAA

C. Abstract of Research Objectives:

The hydroxyl molecule (OH) is a free radical of considerable importance in the photochemistry of the earth's atmosphere. Studies of the middle atmosphere require experimental data on hydroxyl concentration and behaviors for the constraint of theoretical models and for the prediction of future ozone response to stratospheric pollution resulting from man's activities. The experimental work yields measurements of the vertical column abundance of hydroxyl by spectroscopic observations of the absorption of sunlight. The observations include a continuation of the baseline OH measurements, begun in 1976, at the NOAA Fritz Peak Observatory, Colorado (40°N). A second instrument is used to obtain a 2-year series of OH measurements in the tropics (7°N); this instrument is then to be shipped to New Zealand (45°S) for the first southern hemisphere measurements of hydroxyl. A theoretical study of geographic differences and chronological changes in OH behavior will be made in order to gain an improved understanding of processes relating to the global problem of atmospheric ozone.

D. Summary of Progress and Results:

The vertical column abundance of atmospheric OH was monitored at Fritz Peak Observatory, Colorado at times of good atmospheric observing conditions during 1987-1989 except during February and April of 1989. Observations with a second instrument located at the National Weather Service Office on Truk, Federated States of Micronesia were also made during the periods: January-February 1987, June-July 1987, September-October 1987, February-March 1988, September-October 1988, and April 1989.

The total number of independent measurements at Fritz Peak Observatory from January 1, 1988 to July 31, 1989 was 1760. Similarly, 384 independent measurements were made at Truk for the 1987-1989 series. These were approximately 20 minute observation periods with about 15% uncertainty. The Truk instrument was returned to Fritz Peak Observatory on April 30, 1989 for performance check prior to shipping to Lauder, New Zealand for a future 2-year observation series.

The Colorado data base from 1977 through 1988 has revealed significant annual and semi-annual cycles which are amplitude modulated over the 12-year data base. This modulation of the OH seasonal behavior is in phase with solar

activity as described by the sunspot number index. No mechanism for the observed covariance of the OH seasonal behavior with solar activity has yet been identified. These results have been reported to the American Geophysical Union and the American Meteorological Society and have been submitted for publication in Geophysical Research Letters.

The OH observations from Truk are the first column measurements reported for the tropics. These have been examined for possible correlation with the observed tropical middle atmosphere circulations of the quasi-biennial oscillation (QBO) and the semi-annual oscillation (SAO), and for possible effects of heterogeneous reactions which are expected to depend on the tropical tropopause temperatures. The average solar zenith angle dependence of the tropical OH varied approximately as for the Colorado data. The normalized abundances, which eliminate most of the solar zenith angle dependence, exhibited long term variations with the winter-spring abundances significantly above those for summer-fall. The data do not show any clear correlation with tropical circulations. While the observed annual cycle is similar to the Colorado annual cycle, the large abundances are seen to occur at the time of minimum tropopause temperature (-83°C) which also suggest a possible heterogeneous source for OH. A manuscript detailing the Truk results is in preparation.

A theoretical study of a possible mesospheric source for the high-sun enhancement of the Colorado OH data from 1980-1988 has been completed. Results demonstrate that conventional mesospheric photochemistry along with reasonable changes in mesospheric constituents such as ozone and water vapor, temperature, and radiation do not reproduce the observed OH behavior. This study is the subject of a Master's Thesis at Florida Atlantic University by Ms. Yan Liu, and a journal article is in preparation.

E. Journal Publications:

Burnett, Clyde R., Kenneth R. Minschwaner, and Elizabeth B. Burnett, "Vertical column abundance measurements of atmospheric hydroxyl from 26° , 40° , and 65°N ", J. Geophys. Res., 93, 5241-5253, 1988.

Burnett, Elizabeth B., Clyde R. Burnett, and Kenneth R. Minschwaner, "Periodic Behaviors in the Observed Column Abundance of Atmospheric Hydroxyl", Geophys. Res. Lett., 1989. (Manuscript submitted)

A. DIAL SYSTEM FOR STRATOSPHERIC OZONE

B. Principal Investigator : Dr. I. Stuart McDermid

Table Mountain Facility
Jet Propulsion Laboratory
California Institute of Technology
Wrightwood
California 92397-0367

C. Research Objectives

The object of this project has been the establishment of a facility at the JPL-Table Mountain Facility, Wrightwood, California, from which to make long-term atmospheric measurements. The laser remote sensing technique of differential absorption lidar (DIAL) is being used to derive atmospheric ozone concentration profiles. Data will be collected over a long term in order to aid in the detection of trends and changes in the ozone concentration and its vertical distribution. It is anticipated that the JPL-TMF facility could become part of a global network of atmospheric monitoring stations making similar observations. It is also expected that this facility will play an important role in the correlative measurements program related to the Upper Atmosphere Research Satellite (UARS).

D. Progress and Results

Two separate systems are required to obtain the full profile from the ground to 50 km. For the tropospheric part of the profile the lidar system is at the stage of making preliminary test measurements. For the stratosphere, ozone profiles have been obtained on a routine basis since January 1988. During 1988 profiles were measured on 111 separate days. For 1989, 100 profiles have been measured by the end of July. Two extensive inter-comparison campaigns involving a number of ozone measuring systems and techniques have been carried out at the TMF location. Also, a longer term comparison with results from the SAGE II instrument from all of 1988 have been undertaken. The results from these inter-comparisons confirm the ability of the lidar instrument to make precise and accurate measurements of the ozone concentration profile on a regular basis.

E. Publications

I. S. McDermid and S. M. Godin.
Laser Applications in Meteorology and Earth and Atmospheric Remote Sensing,
Eds. M. Sokolowski and D. Killinger, Proc. SPIE 1062, 1989, 225-232.
Stratospheric Ozone Measurements Using a Ground-Based, High-Power Lidar.

I. S. McDermid, S. M. Godin and L. O. Lindqvist.
Applied Optics, submitted January 1989.
Ground-Based Laser DIAL System for Long-Term Measurements of Stratospheric Ozone.

D. A. Haner and I. S. McDermid.
IEEE J. Quantum Electron., submitted July 1989.
Stimulated Raman Shifting of Nd:YAG Fourth Harmonic (266 nm) in H₂, HD and D₂.

I. S. McDermid, S. M. Godin, Pi-Huan Wang and M. P. McCormick.
J. Geophys. Res., submitted July 1989.
Variations in the Stratospheric Ozone Profile During 1988 at 34° N Measured by Lidar and SAGE II.

I. S. McDermid, S. M. Godin, L. O. Lindqvist, T. D. Walsh, J. Burris, J. Butler, R. Ferrare, D. Whiteman and T. J. McGee.
Applied Optics, submitted August, 1989.
Measurement Inter-Comparison of the NASA-JPL and NASA-GSFC Stratospheric Ozone Lidar Systems.

T. J. McGee, R. Ferrare, J. Butler, P. Newman, D. Whiteman, J. Burris, S. M. Godin and I. S. McDermid.
J. Geophys. Res., to be submitted 1989.
Lidar Observations of Ozone Changes Induced by Sub-Polar Airmass Motion Over Table Mountain, 34° N.

A. Ground-Based Lidar Measurements of Stratospheric Ozone The NASA/GSFC Stratospheric Ozone Lidar Trailer Experiment "STROZ LITE"

RTOP #: 147-13-17-20

B. Principal Investigator: Thomas J. McGee
NASA/GSFC
Greenbelt, MD 2071
301-286-5645

Co-Investigators: James Butler, STX Corp.
John Burris, NASA/GSFC
William Heaps, NASA/GSFC

C. Abstract of Research Objectives

The major research objective is the measurement of high precision vertical profiles of ozone between 20-40 kilometers. The precision is such that the instrument should be capable of detecting a small trend (on the order of less 1%/yr.) over a 5-10 year period. A measurement of temperature is also made between 30 and 365 km.

D. Summary

In fiscal 89 two ozone intercomparison campaigns were carried out, both at JPL's Table Mountain Facility in the San Gabriel Mountain just east of Los Angeles, California. In October-November 1988 the GSFC mobile lidar was installed at Table Mountain and a comparison between it and the permanent JPL lidar was made over the course of about 3 weeks. In addition ECC and ROCOZ sondes were launched from Pt. Mugu (about 100 miles from Table Mountain), and these were also a number of SAGE II overflights during the intercomparison. The major result was that the two lidars agreed very well between 20 and 40 km and under certain conditions up to 45-47 km. There were several anomalies noted during the course of the intercomparison which were followed very well by the two lidar. Agreement with the ROCOZ and ECC sondes was also very good however there were several instances showing differences which appear to be due to the spatial and temporal separation of the sondes and the lidars.

In July 1989, a much more formal intercomparison was held at Table Mountain. Again the Stroz Lite instrument was deployed at the Facility along with the JPL lidar. ECC sondes were launched at Table Mountain at the same times that the lidars were taking data. A microwave instrument, a Brewer instrument and a Dobson operated in the Umkehr mode were all in operation during the intercomparison, and were all located at Table Mountain. Additionally ROCOZ sondes were launched from San Nicholas Island (about 150 miles west of Table Mountain) and SAGE II had four overpasses. A preliminary look at the data indicates excellent agreement among the instruments. The GSFC instrument appears to have made excellent measurements between 20 and 42 km.

E. Publications

1. "STROZ Lite: NASA Goddards Stratospheric Ozone Lidar Trailer Experiment," T. J. McGee, R. Ferrare, J. J. Butler, P. Newman, D. Whiteman and J. Burris, NASA Technical Memorandum in Press 1989.
2. "Lidar Observations of Ozone Changes Induced by Sub-Polar Airmass Motion over Table Mountain (34.4°N)," T. J. McGee, R. Ferrare, J. Butler, P. Newman, D. Whiteman, J. Burris, S. Godin and I. S. McDermid, submitted to JGR, 1989.
3. "Measurement Intercomparison of the JPL and GSFC Stratospheric Ozone Lidar Systems," I. S. McDermid, S. M. Godin, L. O. Lindquist, T. D. Walsh, J. Burris, J. Butler, R. Ferrare, D. Whiteman and T. J. McGee, submitted to Applied Optics, 1989.
4. "A Mobile, Differential Absorption Lidar for the Measurement of Stratospheric Ozone and Temperature," T. J. McGee, D. Whiteman, R. Ferrare, J. Butler and J. Burris, submitted to JGR, 1989.
5. "A Lidar Measurement of Ozone in the Presence of a High Loading of Aerosol from the Launch of a Titan 34-D Rocket," T. J. McGee, R. Ferrare, J. Butler, J. Burris and D. Whiteman, submitted to GRL.

Biennial Report on
A MILLIMETER WAVE SYSTEM FOR REMOTE SENSING OF OZONE

Contract NAS5-30104
Jointly Funded by NSF Grant #ISI-8501016

Dr. Alan Parrish, Millitech Corp, Principal Investigator

Objective

The purpose of this work is to develop a millimeter wave spectroscopic instrument for the measurement of ozone in the middle and upper stratosphere. The instrument observes the pressure-broadened spectral lines produced by rotational transitions of stratospheric ozone at 109.559 and 110.836 GHz, and is intended for use in the Network for Early Detection of Stratospheric Change.

Summary

A prototype version of the instrument was put into operation at the Millitech Corporation facility at South Deerfield, Massachusetts, in January, 1989. The next six months were devoted to tests and modifications as needed to prepare a completed instrument for delivery in June of 1989. The instrument was delivered to and is in operation at the Table Mountain Observatory of the Jet Propulsion Laboratory in Wrightwood, California. The instrument participated in the NASA-sponsored Stratospheric Ozone Intercomparison Campaign at Table Mountain from July 19-August 3, 1989.

A collaboration was arranged with Dr. Brian J. Connor of the NASA Langley Research Center for a scientific program using the instrument. Work being done under the resulting grant is described separately in this volume.

Jointly with Dr. Connor, collaborations were arranged with Dr. William J. Wilson of JPL, and Dr. I Stuart McDermid of JPL Table Mountain Observatory to develop procedures for operation and maintenance of the instrument, and analysis of its data. Dr. Wilson's group is responsible for the operation and maintenance of the instrument, with day-to-day on site assistance from Dr. McDermid's group. Data analysis will primarily be performed at NASA Langley Research Center by Drs. Connor and Parrish. This arrangement is intended to serve as a model of a network having additional similar instruments at several field locations with data processed at Langley.

Publications

There were no publications from this task during this period. Preparation of publications regarding the instrument and data from the intercomparison campaign will begin shortly.

RESEARCH SUMMARY FOR
NASA UPPER ATMOSPHERE RESEARCH PROGRAM

1 SEPTEMBER 1989

A. TITLE: Microwave Measurements of Mesospheric Water Vapor

B. INVESTIGATORS/INSTITUTIONS: Dr. Charles L. Croskey
Dr. John J. Olivero
Penn State University
University Park, PA 16802

C. ABSTRACT OF RESEARCH OBJECTIVES:

This research program is focused within three task areas, as follows. The first is to continue a series of ground-based microwave observations of water vapor in the mesosphere from Penn State. This unique data set spans five years and Penn State's is the only dedicated observatory of its kind. The second task is to continue the data analysis and interpretation for a great deal of this water vapor data in archive. The third task is to develop a second, more transportable microwave radiometer which can observe water vapor in the mid- and upper stratosphere as well as in the mesosphere. This second system would be used to obtain observations at other sites, especially different latitudes. It will collaborate in the NASA Network for the Detection of Stratospheric Change. Both radiometers will be used in correlative studies for the NASA Upper Atmospheric Research Satellite (UARS).

D. SUMMARY OF PROGRESS AND RESULTS:

1. The Penn State water vapor observatory has been in operation most of 1988 and 1989 (to date). In 1988, we made observations throughout late summer and early fall for the first time.

2. Most of the water vapor observations from 1984 - 1987 have been analyzed and the results have been presented in AGU meetings; they are being published, see section E. Analysis of these measurements has been addressed to questions of the roles of advective and diffusive transport in minor constituent vertical profiles, as well as the seasonal structure of H₂O. Observations from 1988 and early 1989 have undergone preliminary analysis.

3. The design of the second water vapor radiometer (cooled FET - solid state) is nearly complete and procurement of components is well along.

E. JOURNAL PUBLICATIONS:

1. "Mesospheric Water Vapor Measurements from Penn State: Monthly Mean Observations (1984 - 1987), Richard M. Bevilacqua, John J. Olivero, and Charles L. Croskey, Journal of Geophysical Research, in press, 1989.

2. "The Seasonal Variation of Water Vapor and Ozone in the Upper Mesosphere: Implications for Vertical Transport and Ozone Photochemistry", Richard M. Bevilacqua, Darrell F. Strobel, Michael E. Summers, John J. Olivero, and Mark Allen, Journal of Geophysical Research, accepted for publication, 1989.

BIENNIAL RESEARCH SUMMARY

A. TITLE: Ground-based Monitoring of Water in the Earth's Middle Atmosphere

B. INVESTIGATORS: P. R. Schwartz, R. M. Bevilacqua, and T. A. Pauls
Naval Research Laboratory
Washington DC 20375-5000

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Vienna VA 22180

C. ABSTRACT OF RESEARCH OBJECTIVES:

Water vapor is the primary source of OH and other hydrogen compounds which are important in ozone photochemistry. It is also extremely infrared active and plays a central role in establishing middle atmosphere radiative balance. Finally, under some conditions, it is an excellent tracer of atmospheric motions and may be used to test multi-dimensional models. We have constructed, tested and will soon place in operation a 22 GHz ground-based radiometer for continuous measurements of water vapor in the stratosphere and mesosphere. This instrument has three unique features:

(1) it utilizes an all solid-state receiver based upon a high electron mobility FET (HEMT) amplifier,

(2) its multi-filter spectrometer is a modified version of the system designed for the Microwave Atmospheric Sounder and is thus rugged and ultra-stable, and

(3) it was designed for nearly automatic operation.

The design and construction of the instrument is based upon almost a decade of experience in middle atmosphere radio spectroscopy and utilizes tested and validated retrieval algorithms and techniques. This system will allow, for the first time, measurement of water vapor profile at altitudes of 20-70 km from the ground. An experimental program will be conducted with this instrument to test its performance as a remote system with the ultimate goal of using it as a part of a suite of ground-based middle atmosphere monitors.

D. SUMMARY OF PROGRESS AND RESULTS

This program started in June 1987 and progress during the first year was confined to design, engineering and procurement of the hardware. The following is a chronological summary of progress during 1988-9.

The multi-filter spectrometer filter electronics modules were completed in April 1988. These were a 10 x 40 MHz and 20 x 2 MHz unit (a so-called W/I module) and a 30 x 200 KHz (N module). The board computer processor and data acquisition system was also completed and tested at this time. The software in the processor is identical to the FEB software used in the MAS experiment so that no development was required. A Compaq-plus computer was selected as the central processor for the monitoring system. These units are portable, rugged and sufficiently inexpensive that several spares can be purchased. The processor software is written in PASCAL and contains a menu driven observing program which allows several different observing sequences to be used. Separate software modules control data taking, firing the calibration noise diode, and switching the receiver front-end. These units were bench tested and then used in a field experiment on the roof of Building 209 at NRL in May 1988.

The purpose of the NRL experiment was to test the spectrometer system and software using a radio astronomy receiver borrowed from the Maryland Point

Observatory. The noise temperature of the radio astronomy system was expected to be in the range 200-250K (as opposed to <100K for the final system) so we anticipated testing only the 40MHz and 2MHz filter receivers since the signal-to-noise ratio on the 200KHz filters will be very poor. Several problems were encountered using this set up. (1) The radio astronomy receiver system actually had a noise temperature closer to 300K. (2) The bandwidth of the radio astronomy front-end is limited by a filter which is narrower than the 10x40MHz bandwidth so that some channels receive no signal. (3) A spurious signal from the phase-lock system interferes with the 10x40MHz filters. Never-the-less, atmospheric water vapor spectra were obtained in May 1988. An successful attempt was made to retrieve profiles from these spectra using the software package developed for this purpose. The retrieval technique is described in Bevilacqua et al. 1983 J.Geophys.Res. 88, 8523.

The key hardware elements including the wideband, low loss cryogenic circulator and HEMT amplifier were delivered in the winter 1988-9. The cryogenic HEMT amplifiers for this project were constructed by NRAO. Integration of an amplifier into a dewar also containing the cryogenic circulator switch and a cold balance noise source was completed in April 1989. The remaining receiver components consisting of the mixer, L.O. module and an IF driver module were completed by June 1989 and the entire system moved to a roof top location at NRL for another test. The intention is to carry out tests and atmospheric measurements at NRL to validate performance before moving the system to a final location on Table Mountain in California. The overall system noise performance has been verified and other engineering tasks accomplished but, unfortunately, the poor Washington summer weather has not permitted actual measurements (as of August 1989).

Location of the final receiver system for a long series of experiments at Table Mountain California at a site operated by JPL was discussed with W.J. Wilson, C. Ruf and W. Ricketts of JPL. A plan for siting and operation of both the H₂O system and the millimeter-wave O₃ system constructed by MilliTech at the same location has been agreed upon. The current timetable calls for moving to this site during the first week of October 1989. During the initial stages of this experiment, different sky switching schemes will be investigated including the use of a quasi-optic beam chopper being designed by JPL. Data acquisition will be automated and data stored on floppy disks at the sites. These will be picked up and electronically mailed to NRL by JPL personnel. Processing of data from floppy disks and retrievals will be done periodically at NRL.

E. PUBLICATIONS

The following two publications related to retrieval and interpretation of water vapor data were partially supported by this program:

Bevilacqua, R. M. and Olivero, J. J. "Vertical Resolution of Middle Atmospheric Measurements by Ground-based Radiometry" J.Geophys.Res. 93, 9463 (1988).

Bevilacqua, R. M., Strobel, R. F., Summers, M.E., Olivero, J. J., Allen, M. "The Seasonal Variation of Water Vapor and Ozone in the Upper Mesosphere: Implications for Vertical Transport and Ozone Photochemistry" J.Geophys.Res. accepted for publication.

- A. Development of a UV-Visible Spectrograph and Data Analysis System for Measurements of Stratospheric Trace Gases as Part of a New Global Ground-Based Network for Long-Term Measurements
- B. George H. Mount
Susan Solomon
Arthur Schmeltekopf
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Boulder, CO 80303
- C. The unique property of ozone in absorbing biologically damaging ultraviolet radiation from the sun has motivated a great deal of research directed towards a better understanding of the factors influencing the global distribution and temporal variability of ozone. A new global network for early detection of stratospheric change is being built under NAA/NOAA auspices. We are constructing a new UV-visible spectrograph and data analysis system (which builds on our current system) to measure ozone and nitrogen dioxide and other trace gases in the stratosphere as part of the new global network. The new system consists of a new double spectrograph, new telescope system, and a new state of the art reticon array detector system that surpasses the current reticon array system we are currently using.
- D. Funding was received only for FY 1988. Results for that fiscal year are:
1. optical design of the spectrograph completed,
 2. detailed mechanical design of the spectrograph completed,
 3. optical design of telescope begun,
 4. start of prototype spectrograph construction begun,
 5. prototype data acquisition software begun,
 6. prototype array detector system designed and parts breadboarded.

Millimeter-Wave Ozone Measurements for the Network for the Detection of Stratospheric Change

Co-Principal Investigators:

Dr. Brian J. Connor, NASA Langley Research Center
Dr. Alan Parrish, University of Massachusetts*

Research Objective

The primary research objective is to initiate long-term monitoring of stratospheric ozone with a ground-based millimeter-wave spectrometer, the first of several such instruments projected to be part of the Network for the Detection of Stratospheric Change. The ultimate goal of this monitoring is twofold. First, to detect any secular trend in stratospheric ozone abundance, whether of natural or anthropogenic origin and, second, to provide "ground-truth" validation for existing and future satellite measurements of ozone. With this goal in mind, a more immediate objective is to validate the millimeter-wave measurements by tests of the instrument, internal consistency tests on the data, and most importantly, by intercomparison with all other available ozone measurements. The validation process is expected to lead to refinements in the instrument and its operating procedures and in the data analysis. The final objective is to perform short-term scientific studies with the data, including studies of the ozone diurnal and seasonal variations, and comparison of ozone variations with changes in other geophysical parameters, notably temperature and water vapor.

Progress to Date

The instrument was permanently installed at Table Mountain Observatory in California, in June 1989. We participated there in the Stratospheric Ozone Intercomparison (STOIC) in July 1989. Our results are shown in the figure. Other elements of STOIC were two ground-based lidar instruments, three groups launching ECC balloon sondes, a series of rocketsonde launches, overpasses by the SAGE II satellite, Umkehr observations by both Dobson and Brewer spectrometers, and ground-based observations by the ATMOS instrument. Comparisons between the millimeter-wave, lidars, and two of the ECC series were performed on site by an independent coordinator and were "blind" to the experimenters. The data were released to all the experimenters at the end of the period. These preliminary results show excellent agreement among the five measurements, all of them typically falling within a total range of less than 10 percent between 20 and 40 km. Intercomparison with the rest of the STOIC data set is pending. The millimeter measurements extend up to 64 km; the only other measurements above 50 km are SAGE and the rocketsondes. Thus, comparison of these with the millimeter-wave measurements will be particularly important.

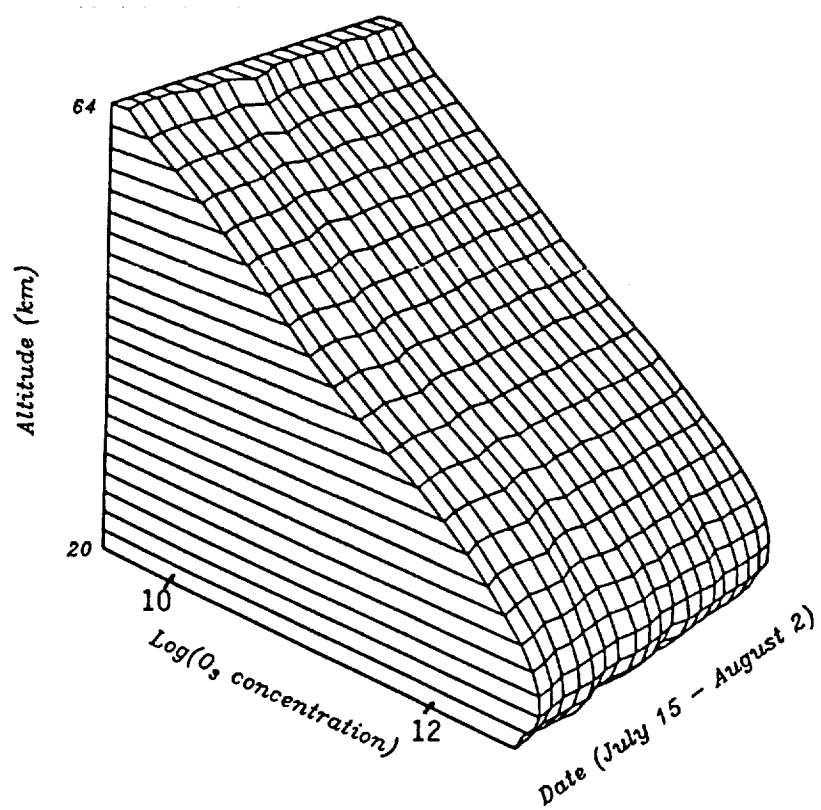
Routine observations are now ongoing; these will allow continuing intercomparisons with SAGE II and one of the lidars, which is permanently on site. The experience gained during STOIC caused us to refine our calibration procedures and identify the need for internal shielding of the millimeter receiver from radio frequency interference. Installation of this shielding is planned for the near future and should allow improvements in the instrument calibration and a higher signal-to-noise ratio, both of which will result in improved measurement precision.

Publications

None

*Also at Millitech Corporation, Deerfield, Massachusetts

TMO Ozone Profiles (1989)



Nighttime ozone measurements during STOIC with the millimeter-wave spectrometer. Units of concentration are cm^{-3} .

N92-14509

A. Title of Research:

Retrieval Methods for Ground-based Millimeter-Wave Measurements
for the Network for the Detection of Stratospheric Change

B. Investigators and Institutions:

Co-Principal Investigators:

Brian J. Connor
Atmospheric Sciences Division
NASA Langley Research Center
Hampton, VA

Richard M. Bevilacqua
E. O. Hulburt Center for Space Research
Naval Research Laboratory
Washington, DC

C. Abstract of Research Objectives:

The fundamental objective is to determine the information available in ground-based millimeter-wave measurements of stratospheric constituent profiles, to identify the optimum method of retrieving this profile information, and to characterize the errors in the final result. A secondary objective is to produce retrieval software for operational use with Network for the Detection of Stratospheric Change (NDSC) measurements of O_3 , H_2O , ClO , and perhaps N_2O .

D. Summary of Progress and Results:

An overall software plan has been formulated. The software design will be modular, consisting of three major components, a forward model for spectral calculations, a generic inverse model for retrievals, and an error analysis section for the characterization of retrieval algorithms.

The millimeter-wave forward model, called Millimeter-wave Emission Temperature of the Atmosphere (META) has been written. It was designed for the specific needs of the ground-based millimeter measurements, and will be used both in a stand alone mode for calculations of spectra and as a subroutine package called by retrieval and error analysis drivers.

Design of the inverse model is presently underway. Various retrieval modules, each incorporating a different algorithm, will be callable by the inverse model.

Finally, tests were performed on existing ozone retrieval programs in support of ongoing NDSC field measurements. The results show that if random spectral errors and retrieval bias errors are considered, accuracy of the retrieved profile is about 5% from 20-50 km, and about 10% from 50-60 km.

E. Publications:

None to date.

D. AIRCRAFT-BORNE MEASUREMENTS

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NASA Upper Atmosphere Research Program: Research Summary 1988-89**A. Title of Research Task**

The ER-2 Meteorological Measurement System

B. Principal Investigator and Institution

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C. Abstract of Research Objectives

The objectives of ER-2 Meteorological Measurement System (MMS) are:

1. To measure the meteorological parameters (pressure, temperature, and the three-dimensional wind vector) accurately.
2. To provide high-resolution data on atmospheric state variables and aircraft flight track to ER-2 investigators on a timely basis.
3. To conduct collaborative research in atmospheric dynamics and chemistry.

D. Summary of Progress and Results

1. MMS successfully participated in the Airborne Antarctic Ozone Experiment (AAOE) based in Punta Arenas, Chile in August and September of 1987.
2. MMS instrumentation (new 20-Mbyte disc, static pressure measurement, power supply, etc.) was improved to minimize single-point failures.
3. Calibrations of the MMS instrumentation (individual sensors, laboratory study of the INS dynamics, system response tests, inflight aircraft maneuvers) were performed. Temperature is accurate to ± 0.3 K, pressure ± 0.3 mb, and wind ± 1 m s⁻¹. Sampling rate is 5 s⁻¹.
4. Much improved software for fast data downloading and postflight processing (incorporating all calibration results) was developed.
5. MMS successfully participated in the Airborne Arctic Stratospheric Expedition (AASE) based in Stavanger, Norway in January and February of 1989.
6. STEP (Stratosphere-Troposphere Exchange Project) MMS 1-Hz and 5-Hz data were revised.
7. AAOE MMS 1-Hz and 5-Hz data were revised.
8. AASE MMS 1-Hz and 5-Hz data were revised.
9. MMS data link via telemetry and real-time computation capability of MMS measurements were developed and successfully demonstrated.
10. Many scientific collaborative activities were conducted and are on-going.

E. Journal Publications

1. Chan, K. R., S. G. Scott, T. P. Bui, S. W. Bowen, and J. Day, Temperature and horizontal wind measurements on the ER-2 aircraft during the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, 1989.
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8. Schoeberl, M. R., L. R. Lait, P. A. Newman, R. L. Martin, M. H. Proffitt, D. L. Hartmann, M. Loewenstein, J. Podolske, S. E. Strahan, J. Anderson, K. R. Chan, and B. Gary, Reconstruction of the constituent distribution and trends in the Antarctic polar vortex from the ER-2 flight observation, *J. Geophys. Res.*, 1989.
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11. Fahey D. W., K. K. Kelly, G. V. Ferry, L. R. Poole, J. C. Wilson, D. M. Murphy, M. Loewenstein, and K. R. Chan, In situ measurements of total reactive nitrogen, total water vapor, and aerosols in polar stratospheric clouds in the Antarctic stratosphere, *J. Geophys. Res.*, 1989.
12. Gandrud, B. W., P. D. Sperry, L. Sanford, K. K. Kelly, G. V. Ferry, and K. R. Chan, Filter measurement results from the Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, 1989.
13. Proffitt, M. H., J. A. Powell, A. F. Tuck, D. W. Fahey, K. K. Kelly, A. J. Kruger, M. R. Schoeberl, B. L. Gary, J. J. Margitan, K. R. Chan, M. Loewenstein, and J. R. Podolske, A chemical definition of the boundary of the Antarctic ozone hole, *J. Geophys. Res.*, 1989.
14. Wilson, J. C., G. V. Ferry, M. Loewenstein, D. W. Fahey, S. D. Smith, K. R. Chan, and K. K. Kelly, Observations of condensation nuclei in the Airborne Antarctic Ozone Experiment: implications for new particle formation and polar stratospheric cloud formation, *J. Geophys. Res.*, 1989.
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18. Several others

ATLAS: Airborne Tunable Laser Absorption Spectrometer for
Stratospheric Trace Gas Measurements

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The ATLAS instrument is an advanced technology diode laser-based absorption spectrometer designed specifically for stratospheric tracer studies. It was first deployed with the Stratosphere Troposphere Exchange Project in 1987. The true fruition of this technique has come with the highly successful acquisition of N₂O tracer data sets on the Airborne Antarctic Ozone Experiment (AAOE, 1987) and the Airborne Arctic Stratospheric Expedition (AASE, 1989). These data sets have proved extremely valuable in themselves for comparison with atmospheric models, as well as in assisting in the interpretation of the entire ensemble of chemical and meteorological data acquired on these two important field campaigns.

During the period covered by this report two major thrusts were underway by the ATLAS research team: one was the analysis and interpretation of the rich data sets acquired during the AAOE field campaign in Punta Arenas, Chile in 1987, the other was preparation for the AASE field campaign to Stavanger, Norway in December-February 1989. The N₂O dynamical tracer data set analysis revealed several important ramifications concerning the polar atmosphere: the N₂O/NO_y correlation, which is now used as a tool to study denitrification in the polar vortex; the N₂O southern hemisphere morphology, showing extensive subsidence in the winter polar vortex; and the value of N₂O measurements in the interpretation of ClO, O₃ and NO_y measurements and of the derived dynamical tracer, potential vorticity. All of these implications of the N₂O data sets are explored in several papers appearing in the Journal of Geophysical Research special issues on AAOE slated to appear late in 1989. Various aspects of these N₂O results were reported by ATLAS team members at the Polar Ozone meeting, Snowmass, May 1988, the Quadrennial Ozone Symposium, Goettingen, FRG, August 1988 and the European Geophysical Society meeting, Paris, Sept. 1988.

The field campaign known as AASE produced an additional large and high quality N₂O data set which has fully occupied the ATLAS team with analysis and interpretation efforts since February 1989. Several papers are now in preparation for a special Geophysical Research Letters issue slated for early 1990 publication.

An intensive ATLAS instrument calibration effort during the first half of 1989 led to an improved characterization of the instrument under field conditions, and a well-based method for establishing the accuracy of the field data from the AAOE and AASE campaigns. The results are incorporated in a manuscript now being prepared for publication.

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Strahan, S. E., M. Loewenstein, J. R. Podolske, W. L. Starr, M. H. Proffitt, K. K. Kelly and K. R. Chan, Correlation of N₂O and Ozone in the Southern Polar Vortex During the Airborne Antarctic Ozone Experiment, J. Geophys. Res. D, Special Issue on AAOE, in press.

AIRBORNE MICROWAVE TEMPERATURE PROFILER INVESTIGATIONS OF ATMOSPHERIC DYNAMICS RELATED TO OZONE DEPLETION

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Research Objectives

Airborne measurements are made of air temperature versus altitude using microwave radiometric remote sensing techniques. The Microwave Temperature Profiler, MTP, covers an altitude region that extends from approximately 2 km below to 3 km above aircraft flight level. Three atmospheric science objectives have been pursued using MTP data taken during flights into the Antarctic and Arctic stratospheric polar vortices: 1) mountain waves in the polar stratosphere have been detected and characterized, 2) calculations of potential vorticity versus latitude have been made possible using the instrument's measurements of air temperature lapse rate, and 3) a component of mesoscale vertical oscillations of air parcels have been identified and characterized for use by polar stratospheric cloud modelers needing realistic cooling rate simulations.

Progress and Results

Mountain waves were found to exist in the stratosphere over the Antarctica Peninsula during the 1987 Airborne Antarctic Ozone Experiment (AAOE). Vertical displacements as great as 600 meters (1200 meter peak-to-peak excursions) were observed in the potential temperature surfaces. The mountain waves were present approximately half the time during flight over the Peninsula and they were not found during flight over the open ocean. Wave amplitude was found to increase with altitude in the region 17 to 22 km in accordance with the predicted relation: $A_1 = A_0 / (P_1/P_0)^{0.5}$. The unexpected presence of mountain waves of such large amplitude in the stratosphere means that air parcels may frequently experience brief cloud forming episodes, which might influence ozone depletion through several possible routes.

Potential vorticity calculations require knowledge of air temperature lapse rate as well as horizontal wind shear. The MTP temperature profiles have provided lapse rate information for the AAOE and 1988/89 AASE (Airborne Arctic Stratospheric Expedition) flights. Penetrations of the polar vortex boundary show the expected changes in potential vorticity, which come entirely from the wind field. Temperature field changes are not noticeable.

Potential temperature surfaces reveal information about vertical displacements of air parcels. Cross-sections showing the altitudes of potential temperature surfaces in a plane parallel to the wind direction can be used to infer vertical velocities, which can be used to infer air parcel heating/cooling rates. MTP data has been used to determine the power spectral density of cooling rate versus frequency of oscillation. An apparently distinct "mesoscale component" of temperature fluctuations appears in such a spectrum. This component produces very large amplitudes of cooling that must be superimposed on simulations of parcel temperature versus time that are derived from synoptic scale weather data. When this is done cooling rates of 200 K/day are common, and during passage through regions disturbed by mountain waves parcels experience cooling rates as high as 2000 K/day. Brief as these cooling rates may be, it is important to determine their impact on polar stratospheric cloud particle size distributions, since only large particles have fall speeds sufficient to "denitrify" layers and thereby permit ClO chemical depletion of ozone.

Journal Publications

Gary, B. L., "Observational Results Using the Microwave Temperature Profiler During the Airborne Antarctic Ozone Experiment," J. Geophys. Res., *in press*

Denning, R. F., S. L. Guidero, G. S. Parks, B. L. Gary, "Instrument Description of the Airborne Microwave Temperature Profiler," J. Geophys. Res., *in press*

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**STRATOSPHERE-TROPOSPHERE EXCHANGE DURING HIGH LATITUDE CYCLOGENESIS
AND LOWER ARCTIC STRATOSPHERE PROPERTIES**

PI'S	Melvyn A. Shapiro NOAA/WPL R/E/WP Boulder, CO 80303	Russell C. Schnell CIRES, CB 449 University of Colorado Boulder, CO 80309
CO-PI's	Patrick J. Sheridan Mike Douglas CIRES, CB 449 Boulder, CO 80309	Nick Bond JISAO/NOAA University of Washington Seattle, WA 98115

Objectives

There are two main objectives to the research:

- 1) The quantification of stratospheric-tropospheric exchange from NOAA WP-3D measurements at higher latitudes and in the Arctic, and;
- 2) The measurement of aerosol properties in the lower Arctic stratosphere as calibrations for concurrent SAGE-II measurements.

This is accomplished through analysis of data collected during 500 WP-3D flight hours (1986-1989) in high latitude marine cyclogenesis systems and in Arctic basin tropopause folding events.

Results to Date

1) Results from the tropopause folding portion of the research are best summarized in graphical form. Figure 1 presents a vertical cross-section of potential temperature (K) and along-front wind component (ms^{-1}) for a NOAA WP-3D study of a marine cold front at 40°N in the North Pacific Ocean, December 9, 1987. Figure 2 shows the ozone concentrations measured in the same frontal structure. In this flight, the NOAA P-3 research aircraft documented the descent of ozone laden stratospheric air down into the eastern Pacific marine boundary layer. This stratospheric tropospheric exchange event occurred in association with a jet stream-frontal zone tropopause folding event.

2) Aerosol light scattering data from 11 NOAA WP-3D research flights into the Arctic spring tropopause and lower stratosphere have been compared to 28 corresponding SAGE-II extinction profiles. Results from this research show that:

- A. There is excellent agreement between the aircraft nephelometer and the SAGE-II extinction measurements above 7 km in the Arctic stratosphere.
- B. The aerosol minimum at the Arctic tropopause, observed in SAGE-II data, is also present in the airborne measurements.

Marine Cold Front
December 9, 1987

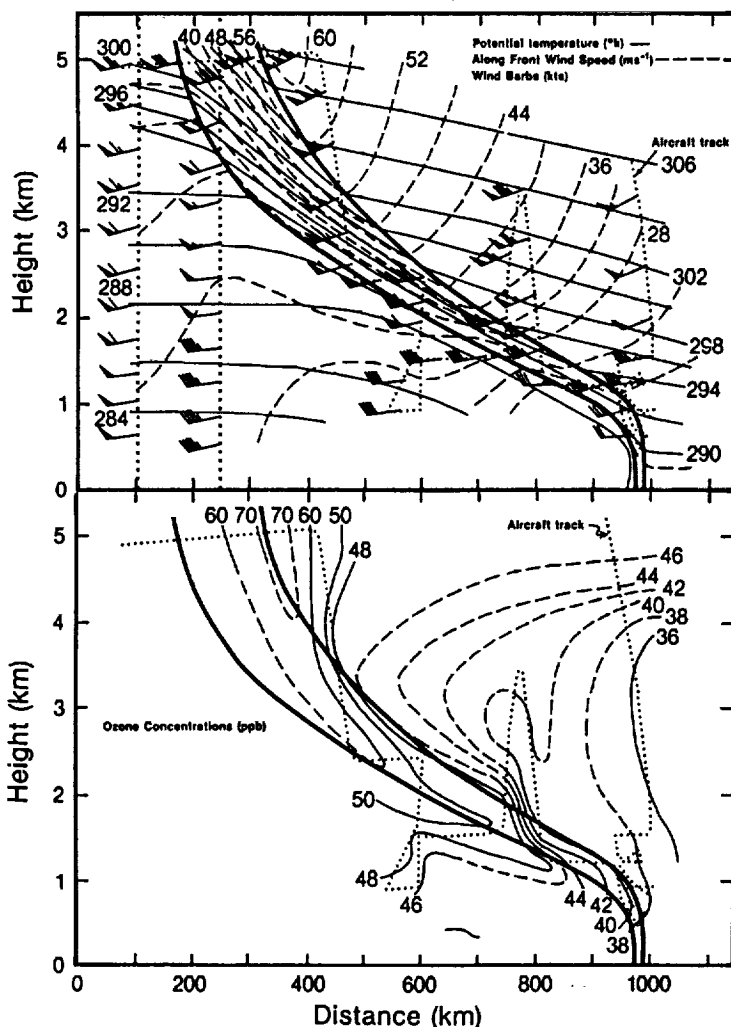


Figure 1. Vertical cross-section of potential temperature (K), along front wind components (ms^{-1}), selected wind barbs (kts) and frontal boundaries (heavy solid lines) for a North Pacific marine cold front tropopause folding event studied with the NOAA WP-3D (aircraft track, dotted line).

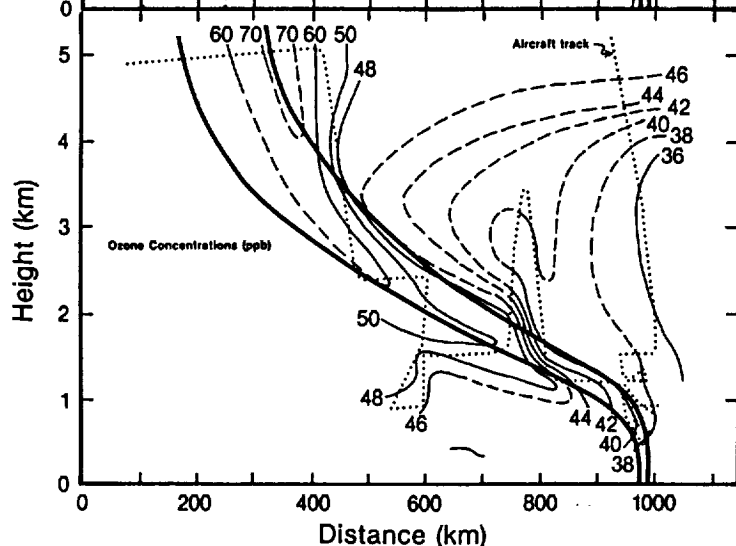


Figure 2. Ozone concentrations (ppb) measured in the fold (Figure 1) illustrating the downward intrusion of elevated concentration of ozone into the marine boundary layer.

Publications

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SUMMARY OF UPPER ATMOSPHERIC RESEARCH

A. Title of Research Task: Ames ER-2 Ozone Measurements.

B. Investigators and Institutions: R. Pearson, Jr., J. F. Vedder, and W. L. Starr (Retired), NASA Ames Research Center.

C. Abstract of Research Objectives: The objective of this research is to study ozone (O₃) in the stratosphere. Measurements of the ozone mixing ratio at 1 s intervals are obtained with an ultraviolet photometer which flies on the ER-2 aircraft.

D. Summary of Progress and Results: The photometer determines the amount of ozone in air by measuring the transmission of ultraviolet light through a fixed path with and without ambient O₃ present. It was completed in 1986 and used in both the Stratospheric Tropospheric Exchange Project and the Airborne Antarctic Ozone Experiment (AAOE). During this reporting period Walter Starr, the former P. I., retired. Richard Pearson, Jr. took over as the new P. I.

In October, 1987, the instrument obtained data on ER-2 flights from Puerto Montt, Chile, to Panama and from Panama to Moffett Field, California.

During February, 1988, it was used in the ER-2 Polar Vortex experiment, which included Harvard's CIO instrument and the Whole Air Sampler (the jointly operated NASA Ames and National Center for Atmospheric Research instrument). The instrument was flown from Moffett Field into the region of maximum wind around the vortex. Both O₃ and CIO increased during the northbound direction of the flight, as reported by Brune et al. (see below). Data obtained during the AAOE were also presented by Starr and Vedder in a poster paper at the Snowmass meeting in May, 1988, and reported in a paper by them accepted by J. Geophys. Res. for the special issue.

The photometer was operated in two piggy back flights, one in late 1988 and the other in early 1989, to acquaint the new P.I. with its operation and to keep it operational pending new support in FY 90.

E. Journal Publications: There are 9 referred publications that utilized data obtained with this instrument and had W. L. Starr or W. L. Starr and J. F. Vedder as co-authors.

Measurements of Ozone in the Antarctic Atmosphere During August and September 1987 (1989): W. L. Starr and J. F. Vedder, J. Geophys. Res.

In Situ Northern Mid-Latitude Observations of CIO, O₃, and BrO in the Wintertime Lower Stratosphere (1988): W. H. Brune, D. W. Toohey, J. G. Anderson, W. L. Starr, J. F. Vedder, and E. F. Danielsen, Science, **242**, 558-562.

Kinetics of O₃ Destruction by CIO and BrO within the Antarctic Vortex: An Analysis Based upon In Situ ER-2 Data (1989): J. G. Anderson, W. H. Brune, S. A. Lloyd, W. L. Starr, M. Loewenstein, and J. R. Podolske, J. Geophys. Res.

Intercomparision of Ozone Measurements Over Antarctica (1989): J. J. Margitan, G. A. Brothers, E. V. Browell, D. Cariolle, M. T. Coffey, J. C. Farnen, C. B. Farmer, G. L. Gregory, J. W. Harder, D. J. Hofmann, W. Hypes, S. Ismail, R. O. Jakoubek, W. Komhyr,

S. Kooi, A. J. Krueger, J. C. Larsen, W. Mankin, M. P. McCormick, G. H. Mount, M. H. Proffitt, A. R. Ravishankara, A. L. Schmeltekopf, W. L. Starr, G. C. Toon, A. Torres, A. F. Tuck, A. Wahner, and I. Watterson, J. Geophys. Res.

Transport into the South Polar Vortex in Early Spring (1989): D. L. Hartmann, L. E. Heidt, M. Loewenstein, J. R. Podolske, J. F. Vedder, W. L. Starr, and S. E. Strahan, J. Geophys. Res.

Implications of AAOE Observations for Proposed Chemical Explanations of the Seasonal and Interannual Behavior of Antarctic Ozone (1989): M. K. W. Ko, J. M. Rodriguez, N. D. Sze, M. H. Proffitt, W. L. Starr, A. J. Krueger, E. V. Browell, and M. P. McCormick, J. Geophys. Res.

Condensed Nitrate, Sulfate and Chloride in Antarctic Stratospheric Aerosols (1989): R. F. Pueschel, K. G. Snetsinger, J. K. Goodman, O. B. Toon, G. V. Ferry, V. R. Oberbeck, J. M. Livingston, W. Verma, W. Fong, W. L. Starr, and K. R. Chan, J. Geophys. Res.

Nitrogen and Chlorine Species in the Spring Antarctic Stratosphere: Comparison of Models with AAOE Observations (1989): J. M. Rodriguez, M. K. W. Ko, N. D. Sze, S. D. Pierce, J. G. Anderson, D. W. Fahey, K. Kelly, C. B. Farmer, G. C. Toon, M. T. Coffey, L. E. Heidt, W. G. Mankin, K. R. Chan, W. L. Starr, J. F. Vedder, and M. P. McCormick, J. Geophys. Res.

Correlations of N₂O and Ozone in the Southern Polar Vortex During the Airborne Antarctic Ozone Experiment (1989): S. E. Strahan, M. Loewenstein, J. R. Podolske, W. L. Starr, M. H. Proffitt, K. Kelly, and K. R. Chan, J. Geophys. Res.

SUMMARY OF UPPER ATMOSPHERIC RESEARCH

A. Title of Research Task: Whole Air Sampler

B. Investigators and Institutions:

James F. Vedder

NASA Ames Research Center

C. Abstract of Research Objectives: Minor constituents play an important role in upper atmospheric photochemistry and serve as tracers in transport and mixing studies in tropospheric-stratospheric exchange processes. Measurements of trace gases are essential to an understanding of the mechanisms by which minor constituents originating in the troposphere, both naturally occurring and anthropogenic, reach the stratosphere; data on tracer distributions thus acquired are important in the development of models for predicting photochemical effects in the stratosphere.

D. Progress and Results: The work reported here is a joint effort of NASA Ames Research Center and the National Center for Atmospheric Research. NCAR is funded separately by NASA Headquarters. Air collected in stainless steel canisters by the automated whole-air sampler (WAS) on the ER-2 and the manually operated sampler on the DC-8 was analyzed by gas chromatography. The data on 8 trace gases (CH_4 , CO , N_2O , CF_2Cl_2 , CFCl_3 , $\text{C}_2\text{F}_3\text{Cl}_3$, CH_3CCl_3 , and CCl_4) reported in the field during the Airborne Antarctic Ozone Experiment based in Punta Arenas, Chile, were validated and presented at the Polar Ozone Workshop in Snowmass, CO, in May, 1988. Subsequently, a paper on these results was submitted to the Journal of Geophysical Research and will appear in a special issue in 1989. Some of the data was used in five other co-authored papers in the special issue.

In February, 1989, the WAS along with the Harvard CIO instrument and the NASA Ames Research Center ozone photometer participated in an ER-2 flight to 61°N latitude in an attempt to enter the polar vortex. Although the ER-2 reached only the maximum wind region of the polar jet stream, interesting results were obtained. The low levels of the measured values of the long-lived trace gases confirmed the expected descent of cold polar air at high latitudes.

The whole-air samplers were again carried aboard the ER-2 and DC-8 during the Airborne Arctic Stratospheric Expedition based in Stavanger, Norway, December to February, 1989. The mixing ratios for 8 trace gases were reported in the field. The results of the analyses of the ER-2 samples were often available within one day of the return of an ER-2 flight. An additional gas chromatograph was operated at the site to measure other trace species of interest. Analyses and validation of the results are continuing.

E. Journal Publications

1) In Situ Northern Mid-Latitude Observations of ClO , O_3 , and BrO in the Wintertime Lower Stratosphere (1988): W. H. Brune, D. W. Toohey, J. G. Anderson, W. L. Starr, J. F. Vedder, and E. F. Danielsen, Science, **242**, 558-562

- 2) Trace Gases in the Antarctic Atmosphere (1989): L. E. Heidt, J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, J. Geophys. Res.
- 3) Transport into the South Polar Vortex in Early Spring (1989): D. L. Hartmann, L. E. Heidt, M. Loewenstein, J. R. Podolske, J. F. Vedder, W. L. Starr, and S. E. Strahan, J. Geophys. Res.
- 4) Lagrangian Photochemical Modelling Studies of the 1987 Antarctic Spring Vortex. Part I: Comparison with AAOE Observations (1989): R. L. Jones, J. Austin, D. S. McKenna, J. G. Anderson, D. W. Fahey, C. B. Farmer, L. E. Heidt, K. K. Kelly, D. M. Murphy, M. H. Proffitt, A. F. Tuck, and J. F. Vedder, J. Geophys. Res.
- 5) Dehydration in the Lower Antarctic Stratosphere During Late Winter and Early Spring, 1987 (1989): K. K. Kelly, A. F. Tuck, D. M. Murphy, M. H. Proffitt, D. W. Fahey, R. L. Jones, D. S. McKenna, M. Loewenstein, J. R. Podolske, S. E. Strahan, G. V. Ferry, K. R. Chan, J. F. Vedder, G. L. Gregory, W. D. Hypes, M. P. McCormick, E. V. Browell, and L. E. Heidt, J. Geophys. Res.
- 6) Nitrogen and Chlorine Species in the Spring Antarctic Stratosphere: Comparison of Models with AAOE Observations (1989): J. M. Rodriguez, M. K. W. Ko, N. D. Sze, S. D. Pierce, J. G. Anderson, D. W. Fahey, K. K. Kelly, C. B. Farmer, G. C. Toon, M. T. Coffey, L. E. Heidt, W. G. Mankin, K. R. Chan, W. L. Starr, J. F. Vedder, and M. P. McCormick, J. Geophys. Res.

Biennial Research Summary

A. **Title of Research Task:** Whole Air Sampler

B. **Investigators and Institutions:**

Leroy E. Heidt National Center for Atmospheric Research

C. **Abstract of Research Objectives:** Minor constituents play an important role in upper atmospheric photochemistry and serve as tracers in transport and mixing studies in tropospheric-stratospheric exchange processes. Measurements of trace gases are essential to an understanding of the mechanisms by which minor constituents originating in the troposphere, both naturally occurring and anthropogenic, reach the stratosphere; data on tracer distributions thus acquired are important in the development of models for predicting photochemical effects in the stratosphere.

D. **Progress and Results:** The work reported here is a joint effort of the National Center for Atmospheric Research and NASA Ames Research Center. NCAR is funded separately by NASA Headquarters. Air collected in stainless steel canisters by the automated whole-air sampler (WAS) on the ER-2 and the manually operated sampler on the DC-8 was analyzed by gas chromatography. The data on 8 trace gases (CH_4 , CO , N_2O , CF_2Cl_2 , CFCl_3 , $\text{C}_2\text{F}_3\text{Cl}_3$, CH_3CCl_3 , and CCl_4) reported in the field during the Airborne Antarctic Ozone Experiment based in Punta Arenas, Chile, were validated and presented at the Polar Ozone Workshop in Snowmass, Colorado, in May, 1988. Subsequently, a paper on these results was submitted to the *Journal of Geophysical Research* and will appear in a special issue in 1989. Some of the data was used in six other co-authored papers in the special issue.

In February, 1989, the WAS along with the Harvard ClO instrument and the NASA Ames Research Center ozone photometer, participated in an ER-2 flight to 61°N latitude in an attempt to enter the polar vortex. Although the ER-2 reached only the maximum wind region of the polar jet stream, interesting results were obtained. The low levels of the measured values of the long-lived trace gases confirmed the expected descent of cold polar air at high latitudes.

The whole-air samplers were again carried aboard the ER-2 and DC-8 during the Airborne Arctic Stratospheric Expedition based in Stavanger, Norway, December, 1988 to February, 1989. The mixing ratios for 8 trace gases were reported in the field. The results of the analyses of the ER-2 samples were often available within one day of the return of an ER-2 flight. Additionally, a mass spectrometer/gas chromatograph was operated at the site to measure other trace species of interest. Analyses and validation of the results are continuing.

E. **Journal Publications**

- 1) Trace Gases in the Antarctic Atmosphere (1989): L. E. Heidt, J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, *J. Geophys Res.*

- 2) Transport into the South Polar Vortex in Early Spring (1989): D. L. Hartmann, L. E. Heidt, M. Loewenstein, J. R. Podolske, J. F. Vedder, W. L. Starr, and S. E. Strahan, *J. Geophys. Res.*
- 3) Lagrangian Photochemical Modeling Studies of the 1987 Antarctic Spring Vortex, Part I: Comparison with AAOE Observations (1989): R. L. Jones, J. Austin, D. S. McKenna, J. G. Anderson, D. W. Fahey, C. B. Farmer, L. E. Heidt, K. K. Kelly, D. M. Murphy, M. H. Proffitt, A. F. Tuck, and J. F. Vedder, *J. Geophys. Res.*
- 4) Dehydration in the Lower Antarctic Stratosphere During Late Winter and Early Spring, 1987 (1989): K. K. Kelly, A. F. Tuck, D. M. Murphy, M. H. Proffitt, D. W. Fahey, R. L. Jones, D. S. McKenna, M. Loewenstein, J. R. Podolske, S. E. Strahan, G. V. Ferry, K. R. Chan, J. F. Vedder, G. L. Gregory, W. D. Hypes, M. P. McCormick, E. V. Browell, and L. E. Heidt, *J. Geophys. Res.*
- 5) Nitrogen and Chlorine Species in the Spring Antarctic Stratosphere: Comparison of Models with AAOE Observations (1989): J. M. Rodriguez, M. K. W. Ko, N. D. Sze, S. D. Pierce, J. G. Anderson, D. W. Fahey, K. K. Kelly, C. B. Farmer, G. C. Toon, M. T. Coffey, L. E. Heidt, W. G. Mankin, K. R. Chan, W. L. Starr, J. F. Vedder, and M. P. McCormick, *J. Geophys. Res.*
- 6) Lagrangian Photochemical Modeling Studies of the 1987 Antarctic Spring Vortex, Part 2: Seasonal Trends in Ozone: J. Austin, R. L. Jones, D. S. McKenna, A. T. Buckland, J. G. Anderson, D. W. Fahey, C. B. Farmer, L. E. Heidt, M. H. Proffitt, A. F. Tuck, J. F. Vedder, *J. Geophys. Res.*

A. Title of Research Task

RADIATIVE FLUX MEASUREMENTS IN THE STRATOSPHERE

B. Investigators and Institution

Francisco P. J. Valero
NASA-Ames Research Center
Earth Systems Science Division
Moffett Field, CA 94035

C. Abstract of Research Objectives

The objective of this research is to determine how the stratospheric tropospheric exchange of water vapor is affected by the interaction of solar (visible) and planetary (infrared) radiation with tropical cumulonimbus anvils. This research involves field measurements from the ER-2 aircraft as well as radiative transfer modelling to determine heating/cooling rates and profiles that directly affect the exchange between the troposphere and the stratosphere.

D. Summary of Progress and Results

The data sets obtained during the 1987 Stratospheric - Tropospheric Exchange Project (STEP) deployment in Australia includes:

- a) Infrared intensities at 6.5 and μm . Field of view: $\sim 8^\circ$ half angle. Measured radiation intensities were referenced to a liquid Nitrogen cooled black body.
- b) Broad spectral bandpass IR fluxes (3 to 40 μm)
- c) Broad spectral bandpass (0.3 - 0.6 μm) solar fluxes

We have used the above data sets to determine cloud optical depths, brightness, temperatures and heating rates. The IR intensities at 10.5 μm are being used for satellite - aircraft intercomparison studies.

E. Journal Publications

Ackerman T. P., Liou, K. N., Valero F. P. J. and Pfister, L., "Heating Rates in Tropical Anvils". Jour. Atm. Sci 45, 1606 (1988).

Liou, K. N., S. C. Ou, F. P. J. Valero and T. P. Ackerman, "Remote Sounding of the Cirrus Cloud Temperature and Optical Depth using ER-2, 6.5 and 10.5 μm Radiometers". Submitted Jour. Atm. Sci (1989).

Valero F. P. J., T. P. Ackerman, W. J. Y. Gore. "Optical Depths and Brightness Temperatures of Tropical Anvils, a Statistical Study". Submitted, Jour. Atm. Sci (1989).

Hammer P. D., F. P. J. Valero and S. Kinne; "Comparative Study of Infrared Radiance Measurements by an ER-2 based Radiometer and the LANDSAT 5 Thematic Mapper (TM6)". Submitted, Monthly Weather Review (1989).

- A. TITLE: Use of radon and cosmogenic radionuclides in the study of stratosphere-troposphere exchange processes
- B. PRINCIPAL INVESTIGATOR: Dr. Mark A. Kritz, Atmospheric Sciences Research Center, State University of New York, Albany, NY 12222

C. RESEARCH OBJECTIVES: To develop and implement, in the context of NASA's Stratosphere-Troposphere Exchange Project (STEP), means of using radon (Rn-222) and cosmogenic radionuclide (Be-7 and P-32) measurements to identify and quantify the exchange of air between the troposphere and the stratosphere. STEP goals include the determination of where, when, how, and at what rate tropospheric air (with its burden of chemical trace constituents) enters the stratosphere, and the identification of the process or processes responsible for the observed extreme dryness of stratospheric air. Because Rn-222, Be-7 and P-32 are subject to the same transport processes as other, chemically reactive atmospheric trace constituents, but have no chemical sources or sinks, the measurement of these and other natural radionuclides has proved to be a valuable component of many field experiments.

D. SUMMARY OF PROGRESS AND RESULTS: The natural cosmogenic radionuclides Be-7 and P-32 (with half-lives of 53 and 14 days, respectively) are produced in the atmosphere (primarily in the stratosphere) by interactions between cosmic rays and nitrogen, oxygen and argon.

The Spring 1984 and Spring 1986 STEP flight series studied transports and troposphere-to-stratosphere exchanges associated with cyclogenesis and tropopause folding in the vicinity of mid-latitude upper tropospheric jets. One of the goals of the mission was to determine whether the entrainment of upper level tropospheric air in conjunction with these processes plays a role in maintaining the vertical gradients of many trace constituents in the lower stratosphere. An analysis of Be-7 measurements made in zones of active mixing near tropopause folds, and in an undisturbed region far from the jet supports this hypothesis, and is presented in publication 1.

In contrast to Be-7 and P-32, radon originates in the earth's crust, where it is produced by the decay of the trace quantities of Ra-226 found in rocks and soils. As a result of its surface-level source, the absence of chemical sources or sinks, and its short (3.8 day) radioactive half-life, radon concentrations are typically large in the continental boundary layer, decrease with height in the troposphere, and are vanishingly small in the stratosphere. Thus the presence of any significant concentration of radon in the stratosphere would be indicative of a recent intrusion of tropospheric air, and the simultaneous observation of high radon and low total water concentrations would be unambiguous evidence of a dehydration process accompanying this exchange.

The decay of radon leads to the formation (via a number of short-lived intermediates) of Pb-210, which has a 22 year radioactive half life. The extensive series of measurements made by the Department of Energy in the High Altitude Sampling Program (HASP) and Project Airstream revealed that there is a large standing crop of Pb-210 in the stratosphere. The observed Pb-210 concentrations were relatively invariant with altitude and latitude, as would be expected from the length of its radioactive half life (22 years) relative to stratospheric residence times. Since the only source of Pb-210 is the decay of radon, it follows that this stratospheric Pb-210 can be accounted for only by a), the transport into the stratosphere of tropospheric Pb-210; or b), the decay, in the stratosphere, of radon entering from the troposphere. As discussed in papers 2 and 4 (see list of publications), there are several lines

of evidence suggesting that the transport of significant quantities of tropospheric Pb-210 to the stratosphere is unlikely, leaving the transport of tropospheric radon as the only likely source for the stratospheric Pb-210.

If this reasoning is correct, it follows that the dominant troposphere-to-stratosphere exchange process (or processes) must carry with them enough radon to account for the 30×10^4 atom/SCM mean Pb-210 concentration observed in the stratosphere. This would imply a mean radon activity in tropospheric air entering the stratosphere of approximately 17 pCi/SCM.

Radon concentrations in the undisturbed upper troposphere are typically on the order of 1 pCi/SCM, about an order of magnitude less than that needed to account for the observed stratospheric Pb-210 abundances. Radon concentrations in the continental boundary layer, on the other hand, are typically on the order of 100 pCi/SCM. Thus the rapid convective ascent of lower tropospheric air in cumulonimbus cells, an exchange mechanism receiving close scrutiny in STEP, would appear to have the potential of bringing the requisite quantity of radon to the stratosphere.

During the STEP field campaign in Darwin, Australia the ER-2 aircraft was directed to regions where meteorological analysis indicated the possibility of active troposphere-to-stratosphere exchange. Elevated radon concentrations were observed in these regions, confirming the occurrence of recent or ongoing intrusions of tropospheric air into the stratosphere. Low radon concentrations were found, as expected, in regions where meteorological analyses indicated an absence of recent troposphere-to-stratosphere exchanges.

While a thorough analysis considering the entire set of meteorological observations and trace constituent measurements must be made before any final conclusions are drawn, preliminary support for the importance of cumulonimbus convection as an exchange mechanism was provided by the radon measurements made during the Darwin field campaign, during which radon concentrations on the order of 20 pCi/SCM were observed in the lower stratosphere downwind of high cumulonimbus turrets.

E. PUBLICATIONS:

- 1) Airmass origins and troposphere-to-stratosphere exchange associated with mid-latitude cyclogenesis and tropopause folding inferred from Be-7 measurements, by M. A. Kritz, E. F. Danielsen and H. B. Selkirk, in press, Journal of Geophysical Research.
- 2) A box model for the exchange of ^{222}Rn and ^{210}Pb between troposphere and stratosphere, by G. Lambert, J. Le Roulley and M. A. Kritz, in press, Tellus.
- 3) Dehydration of the upper tropical troposphere by gravity wave uplift: A case study from STEP, by H. B. Selkirk, L. Pfister, K. Kelly, M. A. Kritz and K. R. Chan, submitted to Geophysical Research Letters.
- 4) Constraints on troposphere-to-stratosphere exchange set by ^{222}Rn measurements made during NASA's STEP experiments, by M. A. Kritz, S. W. Rosner and E. F. Danielsen, to be submitted to the Journal of Geophysical Research.

A. ER-2 Polar Ozone Studies

B. D.W. Fahey, K.K. Kelly, M.H. Proffitt, A. F. Tuck
Aeronomy Laboratory, National Oceanic and Atmospheric Administration,
Boulder, CO 80303

C. Research Objectives

Polar ozone depletion has been addressed by NASA in both the Airborne Antarctic Ozone Experiment(AAOE) and the Airborne Arctic Stratospheric Expedition(AASE). Both missions involved the NASA ER-2 high altitude aircraft instrumented to measure chemical constituents and dynamical variables in the lower stratosphere. The contribution of the NOAA Aeronomy Laboratory has been two fold. First, Dr. Adrian Tuck, acting as Mission Scientist, has played a principal role in the planning and execution of each mission. Second, the total water, ozone, and reactive nitrogen measurements on the ER-2 were provided by instruments that have Laboratory members as Principal Investigators. More than ten flights of the ER-2 were made at latitudes above 60° over each pole in the late winter and early spring. The Arctic mission in early 1989 followed the close of the Antarctic mission by some fifteen months. This interim period was primarily dedicated to data reduction and interpretation and included several group meetings to present preliminary results. The effort has resulted in the publication of a number of peer-reviewed manuscripts in the Journal of Geophysical Research. A similar effort is now underway with the results from the Arctic mission.

D. Summary of Progress and Results

Under the direction of the Project Scientist and with the cooperation of a wide range of participants, both polar missions were a distinct logistic success. Each mission included at least ten flights of both the NASA ER-2 and DC-8 aircraft. As described by Tuck et al.[1989], mission planning required a variety of inputs including consultation with pilots, winds and temperature forecasts aloft and on the surface, satellite and radio sonde data, and atmospheric data from previous flights.

The synoptic and chemical evolution of the Antarctic vortex in 1987 is reconstructed by Tuck[1989] using the aircraft data and satellite and radio sonde data throughout the vortex in the late winter/early spring season. The evidence suggests that cooling, driven by synoptic scale forcing events, produces polar stratospheric clouds that intervene in the homogeneous gas phase chemical balance. The balance is shifted by the heterogeneous production of reactive chlorine and by the removal of total water and reactive nitrogen. In addition, the effects of this perturbed chemistry are transmitted to lower latitudes by the combination of horizontal mixing, diabatic descent, and advective transfer.

The latitude boundary of the chemically perturbed region on each Antarctic flight was noted, in part, by elevated levels of the ClO radical[Proffitt et al., 1989a]. Direct evidence for the removal of both total water and reactive odd nitrogen inside the boundary was obtained by the ER-2 instruments on nearly all flights[Fahey et al., 1989a, Kelly et al., 1989]. The removal is thought to occur by sedimentation of background aerosol particles that grow to sufficient size through condensation of nitric acid and total water. On one flight, ice crystals large enough to have appreciable sedimentation velocities were observed in a region of depleted gas-phase reactive nitrogen. The effects of chemical depletion on ozone were clearly observed from the measurements inside the vortex over the course of the 6 week mission[Proffitt et al., 1989b]. The total water vertical profile measurements outside the vortex provide evidence for the transport of dehydrated air out of the vortex throughout the mission. Evidence for mixing across the vortex boundary was noted in the ClO and ozone measurements near the boundary[Murphy et al., 1989a].

Measurements of nitrous oxide, total water, and reactive nitrogen with

knowledge of potential temperature and potential vorticity were combined to show poleward movement of air near the vortex with on-going diabatic cooling[Proffitt et al., 1989c]. Cooling rates of 1.75K per day were estimated. The data suggest predominantly advective flow of ozone rich air across the boundary and into the ozone hole above 425K potential temperature and accompanying outflow to lower latitudes below this potential temperature.

Measurements of reactive nitrogen and aerosol particles on several flights, combined with temperature, pressure, and laboratory vapor pressure data, were shown to be consistent with the condensation of nitric acid trihydrate on pre-existing sulfate aerosol, several degrees above the local frost point[Fahey et al., 1989b]. The geographical distribution of clouds in the Antarctic as observed with satellite extinction measurements has been analyzed by Watterson and Tuck[1989] to show an asymmetry between the location of dense clouds and temperature minima. The asymmetry is consistent with the restriction of cloud formation in large regions of the vortex because of removal of condensable material and with resupply of condensable material from lower latitudes over a narrow longitude range.

E. Publications

- Fahey, D.W., D.M. Murphy, C.S. Eubank, K. Kelly, M.H. Proffitt, G.V. Ferry, M.K.W. Ko, M. Loewenstein, K.R. Chan, Measurements of nitric oxide and total reactive odd-nitrogen in the Antarctic stratosphere: Observations and chemical implications, *J. Geophys. Res.*, in press, 1989a.
- Fahey, D.W., K.K. Kelly, G.V. Ferry, L.R. Poole, J.C. Wilson, D.M. Murphy, M. Loewenstein, K.R. Chan, In-situ measurements of total reactive nitrogen, total water, and aerosol in Polar Stratospheric Clouds in the Antarctic stratosphere, *J. Geophys. Res.* 94, 11299-11315, 1989b.
- Kelly, K., A.F. Tuck, D.M. Murphy, M.H. Proffitt, D.W. Fahey, R.L. Jones, D.S. McKenna, M. Loewenstein, J.R. Podolske, S.E. Strahan, G.V. Ferry, K.R. Chan, J.F. Vedder, G.L. Gregory, W.D. Hynes, M.P. McCormick, E.V. Browell, L.E. Heidt, Dehydration in the lower Antarctic stratosphere during late winter and early spring, 1987, *J. Geophys. Res.* 94, 11317-11357, 1989.
- Murphy, D.M., A.F. Tuck, K.K. Kelly, K.R. Chan, M. Loewenstein, J.R. Podolske, M.H. Proffitt, S.E. Strahan, Indicators of transport and vertical motion from correlations between in-situ measurements in the Airborne Antarctic Ozone Experiment, *J. Geophys. Res.* 94, 11669-11685, 1989a.
- Murphy, D.M., Time offsets and power spectra of the ER-2 data set from the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, in press, 1989b.
- Proffitt, M.H., J.A. Powell, A.F. Tuck, D.W. Fahey, K.K. Kelly, K.R. Chan, A chemical definition of the boundary of the Antarctic ozone hole, *J. Geophys. Res.* 94, 11437-11448, 1989a.
- Proffitt, M.H., M.J. Steinkamp, J.A. Powell, R.J. McLaughlin, O.A. Mills, A.L. Schmeltekopf, T.L. Thompson, A.F. Tuck, T. Tyler, R.H. Winkler, K.R. Chan, In-situ ozone measurements within the 1987 Antarctic Ozone Hole from a high altitude ER-2 aircraft, *J. Geophys. Res.*, in press, 1989b.
- Proffitt, M.H., K.K. Kelly, J.A. Powell, M.R. Schoeberl, B.L. Gary, M. Loewenstein, J.R. Podolske, S.E. Strahan, K.R. Chan, Evidence for diabatic cooling and poleward transport within and around the 1987 Antarctic Ozone Hole, *J. Geophys. Res.*, in press, 1989c.
- Tuck, A.F., R.T. Watson, E.P. Condon, J.J. Margitan, O.B. Toon, The planning and execution of ER-2 and DC-8 aircraft flights over Antarctica, August and September, 1987, *J. Geophys. Res.* 94, 11181-11222, 1989.
- Tuck, A.F., Synoptic and chemical evolution of the Antarctic vortex in late winter and early spring, 1987, *J. Geophys. Res.* 94, 11687-11737, 1989.
- Watterson, I.G. and A.F. Tuck, A comparison of the longitudinal distributions of polar stratospheric clouds and temperatures for the 1987 Antarctic spring, *J. Geophys. Res.*, in press, 1989.

RESEARCH SUMMARY 1988-1989

A. COUNTING CONDENSATION NUCLEI IN THE LAST YEAR OF THE
STRATOSPHERE-TROPOSPHERE EXCHANGE PROJECT
COOPERATIVE AGREEMENT NCC 2-470

B. James Charles Wilson, Principal Investigator
University of Denver

C. Research Objectives for 1988-1989

1. Finish a paper describing the condensation nuclei results for the Stratosphere-Troposphere Exchange Project (STEP) 1984 missions.
2. Do preliminary analysis on the STEP 1986-1987 data
3. Do preliminary analysis on Airborne Arctic Stratospheric Experiment (AASE) data from the ER-2 Condensation Nucleus Counter (ER-2 CNC) and the NASA owned Passive Cavity Aerosol Spectrometer (PCAS).
4. Report on the performance of the inlet of the PCAS.

D. Progress and Results

1. The STEP 1984 paper has been submitted for publication.
2. STEP 1986-1987 data have been reviewed and the 1987 data have been circulated to investigators.
3. The AASE data are being analyzed and preliminary results have been reported at AASE Science Team meetings.
4. The performance of the PCAS inlet is being analyzed and partial results have been reported.

E. Journal Publications

Wilson, J. C., W. T. Lai, S. D. Smith, Measurements of Condensation Nuclei Above the Jet Stream: Evidence for Cross Jet Transport by Waves and New Particle Formation at High Altitudes, Journal of Geophysical Research, submitted 1989.

RESEARCH SUMMARY 1988-1989

A. COUNTING CONDENSATION NUCLEI IN THE ANTARCTIC OZONE MISSION RESEARCH GRANT NAG 2-458

B. James Charles Wilson, Principal Investigator
University of Denver

C. Research Objectives for 1988-1989

1. Analyze data taken with the ER-2 Condensation Nucleus Counter (ER2-CNC) and other sensors in the Airborne Antarctic Ozone Experiment (AAOE) and publish results.
2. Suggest improvements to the NASA owned Active Cavity Aerosol Spectrometer (ASAS-X) so that it would perform reliably and quantitatively in the Airborne Arctic Stratospheric Experiment (AASE) so that accurate measurements of the background sulfate aerosol would be made in AASE.
3. Improve the sample inlet of the NASA owned Passive Cavity Aerosol Spectrometer (PCAS) so that sampling efficiency would be quantitatively known.
4. Develop field calibration techniques for the PCAS and implement them in the Airborne Arctic Stratospheric Experiment.
5. Operate the ER-2 CNC in the Airborne Arctic Stratospheric Experiment.

D. Progress and Results

1. The AAOE data were analyzed. Polar stratospheric cloud episodes were identified and described. They were classified according to whether or not the size distributions could be explained by existing theory. It was concluded that the data did not permit the denitrification mechanism to be determined. It was determined that sequential, rapid freezing of nitric acid trihydrate and then water such that most or all nuclei grew probably does not account for the denitrification of the polar vortex.

A strong correlation was observed between CN and N_2O . The correlation was positive in the region where the troposphere is the source of CN and was negative in the region of new particle formation. New particle formation was seen to occur throughout the chemically perturbed region and just outside of it.

2. It was recommended that the ASAS-X be replaced with the PCAS. This recommendation was accepted.
3. The sample inlet of the PCAS was modified and instrumented. The sampling efficiency was determined for each point in flight which resulted in a quantitative description of the sulfate aerosol encountered in AASE.
4. The PCAS was calibrated in the field during AASE. The calibrations were used in the development of a calibration which accounts for the refractive index of sulfate aerosol. The field calibrations provide important quality assurance for the PCAS data.

5. The ER-2 CNC was operated in AASE. Data were taken and provided to the project archive for 18 science and ferry flights.

E. Publications

Wilson, J.C., et al., Observations of Condensation Nuclei in the Airborne Antarctic Ozone Experiment: Implications for New Particle Formation and Polar Stratospheric Cloud Formation, *Journal of Geophysical Research*, in press, 1989.

Fahey, D. W. et al. (including J.C. Wilson), In-Situ Measurements of Total Reactive Nitrogen, Total Water and Aerosol in a Polar Stratospheric Cloud in the Antarctic, *Journal of Geophysical Research*, in press, 1989.

1. Title of Research Task

Stratosphere-Troposphere Exchange Project Management

2. Investigators and Institutions

Philip B. Russell, Project Manager, NASA/Ames Research Center

Estelle Condon, Deputy Project Manager, NASA/Ames Research Center

Leonhard Pfister, Project Scientist, NASA/Ames Research Center

3. Abstract of Research Objectives

The purpose of this task is to manage the Stratosphere-Troposphere Exchange Project (STEP). Since the last field program for this project was held in January and February of 1987, this includes holding and planning science team meetings, organizing sessions at conferences devoted to the results and objectives of STEP field programs, putting together special journal issues or special sections of journal issues devoted to the results of STEP, and planning and producing technical memoranda on STEP.

4. Summary of Progress and Results

There were three major field programs devoted to STEP, two midlatitude field programs in Spring of 1984 and Spring of 1986, and a tropical field program in winter of 1987.

The production of a special section of JGR devoted to the STEP 1984 experiment is well underway. This section will include an overview paper written specifically under this research task. Of the six planned papers, three (including the overview paper) have been accepted, one has been submitted but requires major revisions, one has just been submitted, and one will be submitted by 1 November, 1989. The 1986 field experiment was the smallest of the three STEP field programs, and data analysis (and even data reduction) has been held up by the rush of other aircraft field programs since that time. Work is just beginning on the five science flights for the STEP 1986 field program. The project scientist has gathered essential ancillary meteorological data, and has been gathering the aircraft measurements to begin analysis.

Progress on the tropical field program includes: (1) the preparation of satellite imagery including aircraft flight tracks, and distribution to the science team; (2) a science team meeting held in May of 1988; (3) organizing a special session on STEP results during the American Meteorological Society Middle Atmosphere Conference held in San Francisco in April, 1989; (4) planning for a technical memorandum on the tropical phase of STEP which is expected to be published sometime in 1990.

5. Publications

Russell, P. B., E. F. Danielsen, R. A. Craig, and H. B. Selkirk, 1989: The NASA Spring 1984 stratosphere-troposphere exchange experiments: science objectives and operations. Accepted for publication in J. Geophys. Res.

BIENNIAL RESEARCH SUMMARY

- A. TASK # 147-14-20-10 Aircraft Deployment**
TASK # 147-14-30-10 Airborne Arctic Stratospheric Expedition

B. INVESTIGATORS AND INSTITUTIONS

PROJECT MANAGER Estelle Condon, Earth System Science Division
 Ames Research Center, Moffett Field, CA.

PROJECT SCIENTIST Adrian Tuck, NOAA Aeronomy Laboratory,
 Boulder, Col. 80303

DEPUTY MANAGER Steve Hipskind, Earth System Science Division
 Ames Research Center, Moffett Field, CA.

SCIENCE COORDINATOR Brian Toon, Earth System Science Division
 Ames Research Center, Moffett Field, CA.

SCIENCE COORDINATOR Steve Wegener, Earth System Science Division
 Ames Research Center, Moffett Field, CA.

C. RESEARCH OBJECTIVES

The Airborne Arctic Stratospheric Expedition had two primary objectives: 1. To study the production and loss mechanisms of ozone in the north polar stratosphere and 2. to study the effect on ozone distribution of the Arctic Polar Vortex and of the cold temperatures associated with the formation of Polar Stratospheric Clouds (PSC's).

D. SUMMARY OF PROGRESS AND RESULTS

Two specially instrumented NASA aircraft, a high altitude ER-2 aircraft, and a DC-8 flying laboratory were flown over the Arctic region during January and February 1989. The aircraft were operated from Stavanger, Norway. Each aircraft flew a total of 14 flights over the Arctic region to acquire data on the meteorological, chemical and cloud physical phenomena that occur in the polar stratosphere during winter. Measurements were made during the statistically most active period for the formation of Polar Stratospheric Clouds. Extensive systems of polar stratospheric clouds were observed by experiments on both aircraft. The chemical processes which occur in the polar stratosphere during winter were also observed and studied. The data acquired are currently being analyzed in detail and prepared for publication.

E. PUBLICATIONS

The Planning and Execution of the ER-2 and DC-8 Aircraft Flights Over Antarctica, August and September 1987. A.F. Tuck, R.T. Watson, E.P. Condon, J.J. Margitan, O.B. Toon, J. Geophys. Res., in press (1989).

RESEARCH SUMMARY

A. Title of Task: Antarctic Ozone Project

B. Investigators and Institutions: Arlin J. Krueger
Atmospheric Chemistry and Dynamics Branch

C. Abstract

Antarctic springtime total ozone has decreased to record low levels since 1980. Special, quick-look processing of TOMS data is needed to obtain timely information on the state of the ozone hole for use by scientists who are collecting complementary data in the field, as well as for NASA stratosphere program scientists. Raw satellite data are processed and converted to global ozone maps within a day for transmission to the Antarctic and other locations. The total ozone data are compared with atmospheric temperature and pressure data in seeking an explanation for differences in the depth of the ozone hole from year to year. Although the Arctic pole has a different dynamical behavior from the Antarctic, the chemical depletion by chlorine is expected to be similar. The Arctic TOMS data need to be examined for evidence of such depletion even though a feature like the Antarctic ozone hole is not present.

D. Summary of Progress and Results

The development of the 1988 Antarctic ozone hole was observed in quick-look TOMS data from August 21 through November 17, 1988. Contour maps of total ozone were transmitted to McMurdo station for use in planning balloon sounding operations. Color images were made for analysis and domestic distribution.

The 1988 Antarctic ozone hole season began with a series of local deepening in the region just outside the polar night during August. A distorted ozone minimum, displaced from the pole to Pacific longitudes, appeared in September. This minimum failed to deepen significantly in October, resulting in a behavior similar to 1982, prior to the time of the very strong ozone depletions found in 1985 and 1987. By contrast, during September 1987 rapid, substantial total ozone decreases were found and extremely low ozone continued to exist throughout October and November.

The 1989 Airborne Arctic Stratospheric Expedition was supported by real time TOMS data production which began on December 27, 1988 and concluded on February 16, 1989. Quick-look processing continued through mid-March to track evolution of the polar ozone field following the completion of aircraft operations.

The Arctic ozone field was similar to prior years in December and into January. At the end of the month an unusual mini-hole formed over the North sea and Scandinavia, with the center close to Oslo, Norway. This coincided with shifts of the polar vortex and preceded a split of the vortex in Mid-February. The vortex branches then became displaced over Eastern Siberia and Baffin Island where they were easily recognizable on the TOMS maps as deep ozone minima.

The 1989 Antarctic spring will be observed in August - November with quick-look processing and data will be transmitted to Antarctic sites. The Arctic regions may similarly be observed during January - March 1990.

E. Publications

Krueger, A. J., L. M. Penn, D. E. Larko, S. D. Doiron, and P. T. Guimaraes, The 1988 Antarctic Ozone Hole: The Nimbus 7 TOMS Data Atlas, NASA Ref. Publ. 1225, August 1989.

Krueger, A. J., L. M. Penn, D. E. Larko, S. D. Doiron, and P. T. Guimaraes, The 1989 Airborne Arctic Stratospheric Expedition: The Nimbus 7 TOMS Data Atlas, NASA Ref. Publ 1227, July 1989.

Krueger, A. J., R. S. Stolarski, and M. R. Schoeberl, The 1987 Antarctic Ozone Hole: A new record low, Geophys Res. Lett, 15, 1365-1368, 1988.

Krueger, A. J., R. S. Stolarski, and M. R. Schoeberl, Formation of the 1988 Antarctic Ozone hole, Geophys Res. Lett, 16, 381-384, 1989.

A. Title of Research Task: Particle Chemistry Impactor Experiment.

B. Investigators and Institutions:

R.F.Pueschel, Ames Research Center
K.G.Snetsinger, Ames Research Center
G.V.Ferry, Ames Research Center
J.K.Goodman, San Jose State University
S.Verma, TMA/Norcal Inc.

C. Abstract of Research Objectives:

Polar stratospheric cloud particles are collected on impactors and investigated with regard to physical and chemical properties to help explain the importance of heterogeneous chemical reactions for stratospheric ozone depletion.

D. Summary of Progress and Results:

The nitric, hydrochloric and sulfuric acid content of stratospheric aerosol particles collected at 18 km altitude during the 1987 Airborne Antarctic Ozone Experiment (AAOE) was determined. Nitric acid was found to condense at 193.6 ± 3.0 K. Analysis of the July-October 1987 Stratospheric Aerosol Experiment (SAM)II satellite 18 km data shows a threshold temperature 194.5 ± 5.7 K of polar stratospheric cloud (PSC) particle formation. The similar temperature thresholds of both observations strongly suggest that nitric acid is a component of polar stratospheric clouds. This is important for two reasons. First, it proves that chlorine activation takes place at the surface of PSC particles by converting chemically inert chlorine nitrate to chlorine radicals that can react with ozone. Second, if the PSC particles are large enough to settle out from the stratosphere, the possibility of nitric acid removal can result in the denitrification of the stratosphere. This would inhibit chlorine nitrate formation and prolong the catalytic destruction of ozone by chlorine.

E. Journal Publications:

R.F.Pueschel, K.G.Snetsinger, J.K.Goodman, O.B.Toon, G.V.Ferry, V.R.Oberbeck, J.M.Livingston, S.Verma, W.Fong, W.L.Starr, and K.R.Chan, Condensed Nitrate, Sulfate, and Chloride in Antarctic Stratospheric Aerosols, J.Geophys.Res., in press.

J.Goodman, O.B.Toon, R.F.Pueschel, K.G.Snetsinger, and S.Verma, Antarctic Stratospheric Ice Crystals, J.Geophys.Res., in press.

R.F.Pueschel, P.Hamill, and M.P.McCormick, Observational Evidence of Nitric Acid in Polar Stratospheric Clouds, Geophys. Res. Lett., submitted.

SUPPORT OF THE HARVARD ClO/BrO INSTRUMENT FOR THE PREPARATION, EXECUTION, AND DATA REVIEW FOR THE ARCTIC VORTEX MISSION

Investigator and Institution: William H. Brune
Department of Meteorology
Pennsylvania State University
University Park, PA 16802

Abstract

The Airborne Arctic Stratospheric Experiment was designed to determine if the abundances of stratospheric trace species in the wintertime arctic polar vortex were perturbed, as they are in the antarctic polar vortex, and to study the mechanisms responsible for the perturbations. In the absence of ozone depletion, elevated levels of ClO provide one crucial indicator of the change of the polar stratosphere. The Harvard University ClO/BrO instrument, mounted on the NASA ER-2 high altitude aircraft, was used to measure, in situ, the mixing ratios of both ClO and BrO during the AASE mission. The scientific objectives were to explore the abundances of ClO and BrO in a variety of environments near and in the arctic polar vortex, and to determine to what extent ClO abundances are elevated, and why.

Summary of Progress and Results

The Airborne Arctic Stratospheric Experiment was highly successful, and the initial results were released as a statement of preliminary findings. The Harvard ER-2 instrument performed well during the fourteen flights toward the polar vortex from Stavanger, Norway, the four transit flights between Moffett Field, California, and Stavanger, and the five test flights from Moffett Field. One of the most outstanding results was that the ClO abundances inside the polar vortex in mid-February were as high as 1.1 ppbv. This elevated amount of ClO is comparable to amounts seen during the Airborne Antarctic Ozone Experiment in September, 1987. Another result was that ClO abundances were elevated over the entire altitude range surveyed -- 14 to 19 km -- and that the ClO abundances were observed to be greater than 0.5 ppbv for four days in a row in early February. These observations indicate that the air inside the arctic vortex was extensively perturbed.

A rich and diverse mixture of environments was encountered during the AASE flights. ClO and BrO were observed both inside and outside the vortex, in and out of sunlight, and at a variety of altitudes. The variations of these species during changes in these conditions are powerful tools to understanding the photochemical mechanisms, and are being studied by a number of methods.

Publications

Several are in preparation.

NASA Research Summary

A. Measurements of Chemical Constituents in the Arctic Stratosphere

B. M. T. Coffey and William G. Mankin
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307

C. Objectives of this research in 1988 and 89 were for the Optical Techniques project of NCAR's Atmospheric Chemistry Division to use its airborne Fourier transform spectrometer aboard NASA aircraft to measure total column amounts of various chemical species within and in the vicinity of the northern polar vortex, and to analyze results from Arctic and Antarctic field observations.

D. Activities in 1988 and 89 have been divided between field observations and data analysis. In January 1988 we cooperated with the NASA Langley Dual-polarization Aerosol Lidar (McCormick and Poole) to fly a number of missions aboard the NASA Wallops P3 aircraft based in Andenes, Norway. Ten research flights were conducted at latitudes up to 84N. Stratospheric observations with the NCAR spectrometer were made during five flights. Analysis of the 2000 infrared spectra recorded during the program is still underway.

During six weeks in January and February 1989 our experiment was deployed aboard the NASA Ames DC-8 aircraft as part of the Airborne Arctic Stratospheric Expedition (AASE) based in Stavanger, Norway. Eleven research flights were flown and more than 7000 high resolution infrared spectra were recorded covering the spectral range from 700 to 5000 cm^{-1} .

Results from our observations during AASE have been presented at a meeting of the AASE participants and further analysis to derive column amounts of O_3 , NO , NO_2 , HNO_3 , ClONO_2 , HCl , HF , N_2O , CH_4 and Fll are in progress.

Analysis of the large data set from the 1987 Airborne Antarctic Ozone Experiment (AAOE) and meetings to discuss the results have continued during this period and have resulted in the publications listed below.

E.

Airborne measurements of stratospheric constituents over Antarctica in the austral spring 1987: 1. Method and ozone observations, William G. Mankin and M. T. Coffey, accepted by *J. Geophys. Res.*

Airborne measurements of stratospheric constituents over Antarctica in the austral spring 1987: 2. Halogen and nitrogen trace gases, M. T. Coffey, William G. Mankin, and A. Goldman, accepted by *J. Geophys. Res.*

Nitrogen and chlorine species in the spring Antarctic stratosphere: Comparison of models with AAOE observations, J. M. Rodriguez, M.K.W. Ko, N. D. Sze, S. D. Pierce, J. G. Anderson, D. W. Fahey, K. Kelly, C. B. Farmer, G. C. Toon, M. T. Coffey, L. E. Heidt, W. G. Mankin, K. R. Chan, W. L. Starr, J. F. Vedder, and P. McCormick, accepted by *J. Geophys. Res.*

Intercomparison of ozone measurements over Antarctica, J. J. Margitan, G. A. Brothers, E. V. Browell, D. Cariolle, M. T. Coffey, J. C. Farman, C. B. Farmer, G. L. Gregory, J. W. Harder, D. J. Hofmann, W. Hypes, S. Ismail, R. Jakoubek, W. Komhyr, S. Kooi, A. J. Krueger, J. C. Larsen, W. G. Mankin, M. P. McCormick, G. H. Mount, M. H. Proffitt, A. R. Ravishankara, A. L. Schmeltekopf, W. L. Starr, G. C. Toon, A. Torres, A. F. Tuck, A. Wahner, and I. Watterson, accepted by *J. Geophys. Res.*

Airborne observations of chemical constituents in the Antarctic winter stratosphere, William G. Mankin and M. T. Coffey, accepted by *Proceedings of the Quadrennial Ozone Symposium* (Deepak Publishing).

A. Measurements of Chemical Constituents in the Antarctic Stratosphere

B. B. W. Gandrud

National Center for Atmospheric Research

Boulder, Colorado 80307

L. Sanford

Whitworth College

Spokane, WA 99251

C. Research Objectives: 1) To measure the amounts of sulfate and nitrate ion in the particulate phase of the stratospheric aerosol from the NASA ER-2 aircraft. 2) To measure the amounts of nitrate ion in the vapor phase of the sampled air.

D. Progress: The data from the Airborne Antarctic Ozone Experiment has been analyzed and presented. The results show the Antarctic polar vortex to be characterized by background levels of sulfate. The vortex air is depleted in nitrate by comparison with the air outside the vortex but there is still 1 to 3 ppbv of nitrate within the vortex. The vortex air contains more fluoride than extra-vortex air.

The multi-filter sampler was flown on the Airborne Arctic Stratospheric Experiment (AASE). The data from those flights is being processed at present and it will be submitted for publication in the AASE special issue of GRL.

E. "Filter measurement results from the Airborne Antarctic Ozone Experiment" by B.W. Gandrud, P.D. Sperry, L. Sanford, K.K. Kelly, G.V. Ferry and K.R. Chan is in press in the AAOE special issue of JGR.

A. Measurement of Particle Size and Number Concentration with an FSSP-300 on the ER-2

B. D. Baumgardner

J. Dye

B. W. Gandrud

National Center for Atmospheric Research

Boulder, Colorado 80307

L. Sanford

Whitworth College

Spokane, WA 99251

C. Research Objectives: To measure the size and number concentration of particles in the 0.4 to 20.0 micrometer diameter range from the NASA ER-2 aircraft.

D. Progress: A new instrument from Particle Measurement Systems was checked on 4 flights aboard an NCAR aircraft prior to test flights on the ER-2. These flights pointed out problems with the detectors which were rectified before the ER-2 test flights. The instrument was flown successfully on all the Airborne Arctic Stratospheric Experiment (AASE) flights. The data from these flights is being processed at present and will result in 2 papers to be submitted for publication in the AASE special issue of GRL.

E. "Calibration of the Forward Scattering Spectrometer Probe used on the ER-2 during the AAOE" by D. Baumgardner, J.E. Dye and B.W. Gandrud is in press in the AAOE special issue of JGR. Publications from the AASE mission will be forthcoming.

AIRBORNE LIDAR STRATOSPHERIC OZONE AND AEROSOL INVESTIGATIONS

Edward V. Browell
 Atmospheric Sciences Division
 NASA Langley Research Center
 Hampton, VA 23665-5225

Research Objectives:

The objectives of this research are to investigate the distribution of ozone (O_3) and aerosols across the polar regions during the winter and spring periods and to relate these observations to chemical and dynamical processes that can contribute to the chemical perturbation of the polar stratosphere and the possible destruction of O_3 . The distribution and characteristics of stratospheric aerosols and polar stratospheric clouds (PSCs) are required to understand heterogeneous chemical processes that can lead to O_3 depletion, and observations of O_3 variations are important in the direct detection of O_3 depletion and in tracing atmospheric dynamics. An airborne Differential Absorption Lidar (DIAL) system is operated in a zenith mode from the NASA DC-8 aircraft to obtain data on the large-scale spatial variability of O_3 and aerosols/PSC's in the lower stratosphere from about 11-23 km for O_3 and 11-28 km for aerosols. The variability of O_3 and aerosols/PSCs is studied in relation to chemical processes that can produce O_3 depletion and to dynamics in the lower stratosphere that transport gases and aerosols inside the vortex and in some cases, across the edge of the vortex.

Progress and Results:

The airborne DIAL system successfully measured O_3 and aerosol/PSCs distributions in the lower stratosphere during the development of the O_3 hole over Antarctica as part of the 1987 Airborne Antarctic Ozone Experiment (AAOE) and during the 1989 Airborne Arctic Stratospheric Experiment (AASE). The DIAL system was configured to transmit simultaneously four laser wavelengths (301, 311, 600, and 1064 nm) for DIAL measurements of O_3 and for multiple wavelength aerosol backscatter measurements. During the AAOE a total of 13 long-range flights on the NASA DC-8 aircraft were conducted between August 28 to September 29, 1987. Large-scale cross sections of O_3 distributions were obtained with the airborne DIAL system during the formation of the O_3 hole in the polar vortex over Antarctica. DIAL measurements showed that the primary region of O_3 depletion was between 15-22 km inside the polar vortex. Over the period of the AAOE, the average O_3 concentration at high latitude ($>75^\circ S$) decreased by more than 50 percent. Polar stratospheric clouds were detected in thin layers up to an altitude of ~ 21 km in regions of low temperatures (typically ≤ 195 K). Many of the PSC's were found to be very large in vertical and horizontal extent. Some of the larger PSC's extended over 5 km in altitude with considerable vertical structure. The horizontal extent of the larger PSC's was greater than 10 degrees in latitude (>1000 km). The PSC's are associated with the heterogeneous chemistry that converts nonreactive chlorine gases into reactive forms that can catalytically destroy O_3 . The data provided by the airborne DIAL system during the AAOE have been used in numerous collaborative studies of the chemistry and dynamics of the O_3 hole, and they are reported in the special AAOE issue of the Journal of Geophysical Research.

The Airborne Arctic Stratospheric Experiment was conducted from Stavanger, Norway, between January 2 to February 15, 1989, to investigate the conditions leading to possible O_3 destruction in the wintertime Arctic stratosphere. The airborne DIAL system was operated from the DC-8 in long-range flights over the Arctic. In addition to the O_3 and multiple-wavelength aerosol backscatter measurements made during the AAOE, simultaneous aerosol depolarization measurements were made at 622 and 1064 nm. Large-scale distributions of O_3 and PSC's were measured with the DIAL system on 18 flights into the polar vortex. The O_3 distribution clearly indicated the edge of the polar vortex, and it was also an effective tracer for dynamical processes. The primary O_3 layer inside the vortex extended from 14-23 km with a peak at about 18 km. PSCs were observed on almost all missions between January 6-February 3 in regions of low temperatures (188-195 K) between 15-26 km. Two types of PSCs thought to be nitric acid trihydrate were observed. Water ice PSCs were observed in limited regions having even lower temperatures (<188 K). There was no coincident correlation between the presence of PSCs and variations in the O_3 concentration. Ozone data obtained on the last two AASE flights indicated large regions of reduced O_3 concentrations which were spatially correlated with the chemically perturbed region inside the vortex. Investigations are still in progress to determine if this O_3 decrease was due to chemistry or a large-scale warming of this region of the vortex. The chemical perturbation of the Arctic stratosphere was found to be very similar to the conditions found during the 1987 AAOE. Airborne DIAL O_3 and aerosol/PSC data are being used in many ongoing investigations related to the dynamics of the polar vortex, characteristics of the PSCs, and the development of the chemically perturbed conditions during the Arctic winter.

Journal Publications:

Browell, E. V., Differential absorption lidar sensing of ozone, Proceedings of the IEEE, 77, 419-432 (1989).

Kelly, K. K., A. F. Tuck, D. H. Murphy, M. H. Proffitt, D. W. Fahey, R. L. Jones, D. S. McKenna, M. Loewenstein, J. R. Podolske, S. E. Strahan, G. V. Ferry, K. R. Chan, W. D. Hypes, M. P. McCormick, and E. V. Browell, Dehydration in the lower Antarctic stratosphere during the late winter and spring, 1987, In press, J. Geophys. Res., 94, Aug. 1989.

Kinne, S., O. B. Toon, G. C. Toon, C. B. Farmer, E. V. Browell, and M. P. McCormick, Infrared measurements of the size and composition of particles in polar stratospheric clouds with the JPL MARK-IV interferometer, In press, J. Geophys. Res., 94, Aug. 1989.

Ko, M., J. Rodriguez, N. D. Sze, A. Krueger, M. Proffitt, W. Starr, E. Browell, and P. McCormick, Implications of AAOE observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone, In press, J. Geophys. Res., 94, Aug. 1989.

Margitan, J., G. A. Brothers, E. V. Browell, et al., Intercomparison of ozone measurements over Antarctica, In press, J. Geophys. Res., 94, Aug. 1989.

McKenna, D. S., R. L. Jones, J. Austin, E. Browell, M. P. McCormick, A. J. Krueger, and A. F. Tuck, Diagnostic studies of the Antarctic vortex during the 1987 Airborne Antarctic Ozone Experiment: Ozone mini-holes, In press, J. Geophys. Res., 94, Aug. 1989.

N92-14519

- A. TITLE OF RESEARCH TASK: Airborne Aerosol Lidar (RTOP 147-14-34-79)
- B. INVESTIGATORS: Lamont R. Poole and M. Patrick McCormick
Atmospheric Sciences Division
NASA Langley Research Center
Hampton, VA 23665
- C. ABSTRACT. The objectives of this research are: (1) to analyze dual-polarization lidar measurements of aerosols and polar stratospheric clouds (PSCs) obtained aboard the NASA Ames DC-8 aircraft during the 1989 Airborne Arctic Stratospheric Expedition (AASE); and (2) to combine lidar, SAM II, and other AASE data with theoretical modeling calculations to investigate PSC characteristics.
- D. SUMMARY OF PROGRESS AND RESULTS. The Langley dual-polarization aerosol lidar system was successfully integrated aboard the Ames DC-8, and measurements of stratospheric aerosols and PSCs were obtained on all AASE flights (14 Arctic missions and 2 ferry flights). In addition, aerosol and PSC measurements made during AASE by the satellite-borne SAM II sensor were transmitted daily (in both graphical and digital form) to the experiment site in Stavanger, Norway, to assist in mission planning. Final analysis and archival of the AASE SAM II data were completed in April 1989. Preliminary analysis of lidar data from all AASE Arctic missions has been completed, and follow-on studies of 4 Arctic missions are currently in progress. Comparisons of opportunity have been made between AASE lidar and SAM II measurements to study the spatial and temporal variability of PSC properties. A conceptual model for generic classification of the dual-polarization lidar observations has been developed and is being used with theoretical calculations and available meteorological data to investigate PSC formation and growth mechanisms. PSCs were also observed over Northern Europe (near latitude 50N) from Jan. 31-Feb. 2, 1989, by the spaceborne SAGE II sensor; analysis of these multi-wavelength PSC extinction data is in progress. Manuscripts are in preparation (for the AASE special issue of Geophysical Research Letters) to present the lidar and SAM II observations and their comparisons of opportunity, the conceptual lidar data classification model, and the SAGE II PSC observations.
- E. JOURNAL PUBLICATIONS. None (manuscripts in preparation)

TITLE OF RESEARCH TASK: IN SITU OZONE MEASUREMENTS FOR THE AIRBORNE ARCTIC STRATOSPHERIC EXPERIMENT

INVESTIGATOR: Dr. Gerald L. Gregory
NASA Langley Research Center
Hampton, VA 23665-5225

ABSTRACT OF RESEARCH OBJECTIVES:

The research provided in situ ozone measurements onboard the NASA Ames DC-8 research aircraft during the January/February 1989 Airborne Arctic Stratospheric Experiment. The Ames DC-8 and ER-2 aircraft performed extensive sampling of the Arctic stratosphere and troposphere in a program designed to investigate those factors important in ozone depletion in the Arctic during times when the polar vortex and meteorology are conducive to the formation of polar stratospheric clouds and/or an Arctic ozone hole. The DC-8 ozone instrument complement included in situ measurements for H₂O, NO, NO₂, NO_y (gas), NO_y (particulate), as well as remote sensors for measuring the vertical distribution and column density of ozone above the aircraft altitude. The in situ data (ozone, water vapor, and nitrogen species) at the aircraft altitude provide a definition of tropospheric conditions in the vicinity of the polar vortex and polar stratospheric clouds. Defining tropospheric conditions will assist in the understanding of the chemistry of both the stratosphere and troposphere and the extent to which polar stratospheric clouds affect the chemistry of transported air. Currently, little data are available on the chemical composition (stratosphere and troposphere) of air masses which have had encounters with polar stratospheric clouds.

SUMMARY OF PROGRESS AND RESULTS:

The in situ ozone package was successfully flown on all 19 of the AASE missions. Data have been archived and made available to the various investigators. Results show a good correlation of the ozone data among the various instrument platforms (ER-2, DC-8, sonde launches). Comparison of the ozone and nitrogen data suggest that ozone/nitrogen oxide ratios are similar to those observed in the stratosphere. Data also suggest that the high gas phase NO_y mixing ratios can be explained by the precipitation and evaporation of particulate phase NO_y from the higher altitudes. Analyses of these data are continuing.

JOURNAL PUBLICATIONS:

Gregory, G. L., W. D. Hypes, L. S. Warren, A. D. Tuck, K. K. Kelly, and A. J. Krueger, Tropospheric ozone in the vicinity of the ozone hole: 1987 Antarctic Ozone Experiment, accepted J. Geophys. Res., 1989.

A. DC-8 Mission Planning (Task 147-14-51-10)

B. Investigators and Institutions

P. I. Dr. Owen B. Toon, Earth System Science Division, NASA Ames Research Center, Moffett Field, Ca.

C. Objective:

A number of tasks needed to be performed to operate the DC-8 aircraft in the Arctic Ozone Expedition during January and February of 1989. These included development of improved navigational computer programs and performing advanced planning for flight tracks. The missions required further work in the field to plan flight tracks and to establish a data archive. Further work is needed to see that data collected during the expedition are properly reduced.

D. Progress and Results:

The DC-8 aircraft was successfully operated during the deployment phase of the Arctic Ozone Expedition. Data were collected by the investigators revealing the presence of extensive systems of polar stratospheric clouds. The data also showed the evolution of the chlorine and nitrogen chemistry within the Arctic vortex. A navigational computer code was improved so that the DC-8 navigators could perform their function more efficiently. This code was placed upon a computer system that would be accessible to the DC-8 experimenters. A DC-8 archive was initiated for use of the investigators after the mission. Editorial work was done to help with the Journal of Geophysical Research special issue for the Antarctic mission. We are working to help interpret aerosol data taken from DIAL one of the aerosol lidars on board the DC-8. The DC-8 archive will be completed and distributed to the DC-8 investigators.

E. Publications:

The Planning and Execution of ER-2 and DC-8 Aircraft Flights Over Antarctica, August and September 1987. A.F. Tuck, R.T. Watson, E.P. Condon, J.J. Margitan, O. B. Toon, J. Geophys. Res. in press (1989).

E. ROCKET-BORNE MEASUREMENTS

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RESEARCH SUMMARY

A. Title: Measurement of the Absolute Solar UV Irradiance and Variability

B. Principal Investigator: James E. Mentall
NASA/Goddard Space Flight Center
Greenbelt, MD 20771
(301) 286-8959

C. Abstract:

Radiation in the wavelength interval 150-350 nm initiates chemical reactions in the lower mesosphere and the stratosphere through the photodissociation of ambient molecular species. This experiment measures the total solar irradiance, above the Earth's atmosphere, in this wavelength interval, using three spectrometers. Measurements are made from rockets on a once-a-year basis and are used with satellite observations to determine both the absolute irradiance and the long term variability of the sun in the UV. A fourth spectrometer is being added to the payload to measure the emission in the Hydrogen Lyman- α emission at 121.67 nm.

D. Summary of Progress and Results:

After the next flight, which is scheduled for mid-January of 1990, measurements will have been obtained over a complete solar cycle. Over the history of this experiment the absolute error in measuring the solar flux from has been reduced from approximately $\pm 15\%$ to $\pm 5\%$. Data from these rocket flights have been used, along with the results from other experimenters, to determine the absolute value of the solar irradiance in the UV. Observations over the descending portion of the last solar cycle show that the long term variability of the sun is of the same order as short term variability, i.e., 15% at 150 nm and decreasing to only a few percent at 200 nm.

E. Publications:

Mentall, J. E. and D. E. Williams, "Solar Ultraviolet Irradiances on December 7, 1983 and December 10, 1984," J. Geophys Res. 93, 735, 1988.

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Sounding Rocket Studies of CO₂, N₂O, CH₄, and Other Trace Constituents in the Upper Stratosphere and Mesosphere

E. C. Zipf and P. W. Erdman
University of Pittsburgh
Pittsburgh, PA 15260

ABSTRACT

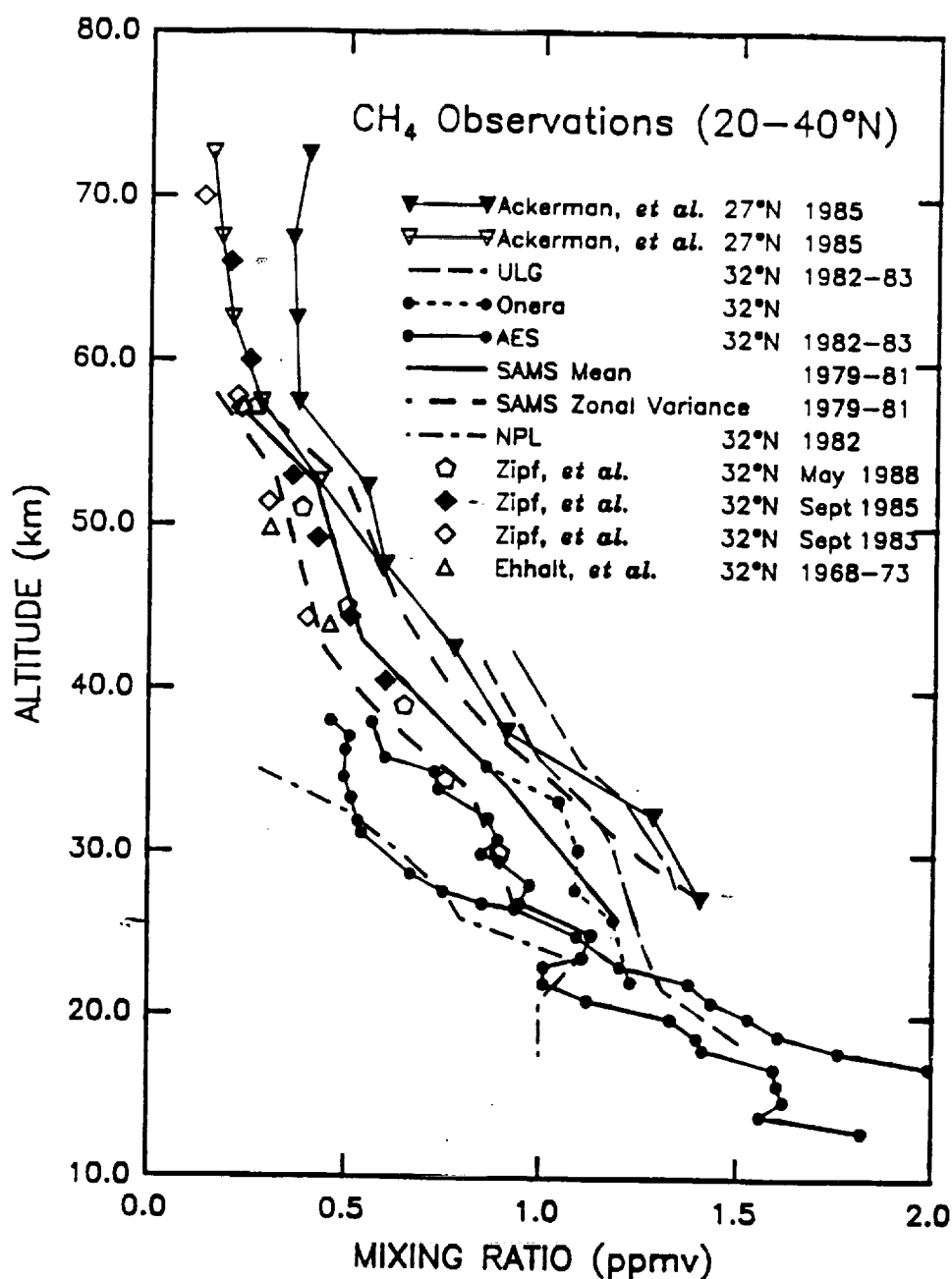
A rocket-borne, cryogenic whole-air sampler [CWAS] is used to investigate the sources and sinks of CO₂, N₂O, NO, CH₄ and other minor constituents in the middle atmosphere from 30-80 km. The atmospheric samples are collected on gold-plated surfaces maintained at ~15°K by on-board CTI-8 closed-cycle helium refrigerators. The cold fingers are located in specially prepared stainless steel canisters and are exposed to the atmosphere through pneumatically actuated UHV valves. The CWAS payload collects samples on the upleg of the flight in the ram position. The large samples collected in this manner (~2-15 std-liters) are concentrated further after recovery so that the density of the final samples analyzed by optical, mass spectrometer, and gas chromatographic techniques is ~10⁵ times the ambient values. Mixing ratio values with a precision better than ±1% can be obtained by this technique over the entire altitude range with a resolution, Δz, varying from 0.5-3 km. CO₂, CH₄ and N₂O mixing ratio profiles and data on the altitude variation of the ¹²C/¹³C, ¹⁸O/¹⁶O, and ¹⁸O/¹⁷O isotope ratios in the middle atmosphere have been obtained from Nike-Orion flights launched from the White Sands Missile Range (WSMR) (32°N) and from Churchill Research Range (CRR), Churchill, Manitoba (58°N). During this summary period [1988-1989], the operational range of the CWAS payload was extended down to 30 km in order to overlap the observation range of high-altitude balloons and to permit careful cross-comparison measurements. Trace constituent data in the arctic air mass above CRR following the major solar flare during March 1989 were also obtained as part of NASA's CAMPAIGN 89.

PROGRESS REPORT

The CWAS payload was originally designed to provide trace constituent data in the altitude range 40-80 km. In-situ tests were actually carried out up to 110 km in order to determine how high in the atmosphere this technique would provide high accuracy mixing ratio data. 80 km now appears to be a working upper limit for the skimmers (diameter 3.5 cm presently being used). The lowest practical sampling altitude depends, in a complex way, on vehicle, nose cone, and cooling-power constraints. During May 1988, two successful launches of the CWAS payload from the White Sands Missile Range [WSMR] demonstrated that very large samples (~15 std liters) could be obtained readily at altitudes as low as 28 km. A large number of fluorocarbon compounds have been detected in these low altitude samples in addition to the other minor constituents (CO₂, CH₄, NO, and N₂O) that have been the focus of the higher altitude CWAS measurements. The large size of the samples has permitted a detailed study of the isotope ratios of the principal

atmospheric constituents as well as the measurement of the $^{12}\text{C}/^{13}\text{C}$ ratio for CO_2 and CH_4 .

The samples from ten CWAS launches have now been analyzed in detail. Some of the methane results are shown in the figure where they are compared with the body of CH_4 data obtained at mid-latitudes by earlier balloon, shuttle, and satellite experiments.



The CWAS results for CH_4 , N_2O , and CO_2 will be published in the near future.

Biennial Research Summary

A. Title: Rocket Temperature Soundings

B. Investigators and Institutions:

Francis J. Schmidlin
NASA/GSFC/Wallops Flight Facility

C. Abstract:

Provide rocket-borne measurements of temperature and wind. These data are used to obtain a better understanding of the processes that control the chemical and dynamical behavior of the stratospheric region, to monitor temperature trends and detect changes, to verify and monitor remote measurements (ground- and satellite-based), to provide direct wind measurements for verification of the balance wind derived from remote measurements, and to provide density measurements for large space vehicle operations.

D. Progress and Results Summary:

During the period October 1988 and June 1989, twenty-six measurements of temperature and wind were obtained using the Super Loki Datasonde rocket instrument. Eight system failures occurred between March and June, and eleven payloads were rejected for various reasons. The failures and the rejected systems impacted the continuity of the desired one per week launch schedule. Since July, there have been no launchings because of lack of rocketsonde systems. It was assumed that the total number of systems would be sufficient until newly procured flight hardware could be delivered during September. It is important that the inventory contain enough flight systems so that the one per week launch schedule can be maintained. So far, funds have been insufficient to meet this objective.

Some analysis of the existing rocketsonde data available from all the launch ranges has been used to study temperature trends. This required considerable review and quality control of the data files, and in some cases a complete re-evaluation of the data needed to be made. The temperature trend since 1969 has been downward, however, before an accurate value can be fixed we must consider the trends being displayed by other measurements systems such as satellite retrieved temperatures. This involves much more work, but we have TOVS data in hand and are beginning to examine how well the two methods (rocket and satellite) agree. We have also spent some effort in looking at the falling sphere technology. The sphere has been found to provide quite accurate temperature measurements between 85 km and the point of sphere collapse (near 35 km). The sphere uses the gas equation to determine temperature from density and pressure. Density is the basic parameter calculated by solving the equations of motion for the falling sphere; radar position data are used. For various reasons (i.e., wrong sphere weight is a major source of error) the density data may be in error up to 5-10 percent; this density value is used to calculate a pressure. Any error in density appears as a similar magnitude error in pressure so that solving the gas equation cancels the error leaving an accurate value of temperature. Consequently, given a linear error in density the temperatures retrieved will be quite accurate between 35-85 km. This has been demonstrated theoretically, with computer simulation, and with actual flight comparisons between spheres and Datasondes, and was presented in a paper given at the 9th ESA Symposium.

E. Publications:

Schmidlin, F. J., H. S. Lee, and W. Michel, 1989: Evidence for accurate temperatures from the inflatable falling sphere. Proceedings of 9th ESA Symposium on European Rocket and Balloon Programs.

Luebken, F., U. von Zahn, A. Manson, C. Meek, U. Hoppe, F. J. Schmidlin, et al, 1989: Mean state densities, temperatures, and winds during the MAC/SINE and MAC/EPSILON campaigns. J. Atmos. Terr. Phys.

Goldberg, R. A., D. Fritts, A. Chou, J. Barcas, and F. J. Schmidlin, 1988: Studies of high latitude mesospheric turbulence by radar and rocket - 1: Energy deposition and wave structure. J. Atmos. Terr. Phys.

Blood, S., J. Mitchell, C. Croskey, A. Raymund, E. Thrane, T. Blix, U. Hoppe, D. Fritts, and F. J. Schmidlin, 1988: Studies of high latitude mesospheric turbulence by radar and rocket - 2: Measurements of small scale turbulence. J. Atmos. Terr. Phys.

F. INSTRUMENT DEVELOPMENT

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BALLOON-BORNE MEASUREMENTS OF POLAR STRATOSPHERIC OZONE

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NASA Goddard Space Flight Center
Wallops Flight Facility
Wallops Island, VA 23337

Research Objectives:

The objective was to provide high-resolution measurements of the vertical structure of stratospheric ozone at high northern and southern latitudes, as part of a series of studies of stratospheric ozone losses over polar regions.

Summary of Progress and Results:

Fifty-seven balloon-borne ozonesonde soundings were conducted from Palmer Station, Antarctica (65°S, 64°W), between September 3 and October 31, 1988. Although the 1988 austral-springtime ozone depletion over most of Antarctica was generally not as deep as during the record year of 1987, much of the activity centered over Palmer Station. The losses in total ozone overburden at this location were nearly as great during the 1988 season as during 1987. Starting at about 325 DU in early September, the column ozone amount had dropped to 200 DU before mid-October.

While the decrease in column ozone amounts over Palmer Station during 1988 was similar to that of 1987, the vertical profiles had quite different characteristics. During 1987 there were layers, at altitudes of about 17 km, in which ozone depletion was essentially complete - over 95 percent. Such deeply-depleted layers were absent over Palmer Station in 1988.

As an element of the AASE mission, thirty-seven ozonesonde soundings were made from Lerwick, Shetland Islands (61°N, 2°W), between January 7 and February 13, 1989. During this same time period, the Danish Meteorological Institute launched three sondes per week from each of two sites in East Greenland, using sondes provided by NASA. These data are currently being analyzed.

Journal Publications:

Torres, Arnold L., and George Brothers, "Ozone Profiles over Palmer Station, Antarctica," submitted to Journal of Geophysical Research, 1989.

Margitan, J. J., G. Brothers, E. V. Browell, D. Cariolle, M. T. Coffey, J. C. Farman, C. B. Farmer, G. L. Gregory, J. W. Harder, D. J. Hofmann, W. Hypes, S. Ismail, R. O. Jakoubek,

W. Komhyr, S. Kooi, M. H. Proffitt, A. R. Ravishankara, A. L. Schmeltekoph, W. L. Starr, G. C. Toon, A. Torres, A. F. Tuck, A. Wahner, and I. Watterson, "Intercomparison of Ozone Measurements over Antarctica," J. Geophys. Res., in press.

TITLE : DEVELOPMENT OF A FAST RESPONSE ATMOSPHERIC METHANE MONITOR FOR THE NASA ER-2 AIRCRAFT

INVESTIGATORS : J. B. McManus, P.L. Keabian, C.E. Kolb

**Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821**

ABSTRACT OF RESEARCH OBJECTIVES :

It has been the objective of this project, under contract number NASW-4345, to develop the core of an infrared-laser based atmospheric measurement instrument that is intended for eventual deployment on the NASA ER-2 high altitude research aircraft. The goal of this phase of development is to construct and test the optical core of the instrument, which will demonstrate the basic instrument performance in terms of sensitivity, stability and automatic operation. The ARI Stratospheric Methane Monitor is based on a magnetically broadened HeNe laser operating at 3.39 microns, which is coincident with a methane absorption line. The instrument utilizes a compact, fast flow response, multipass absorption cell, with over 50 meters of pathlength. The instrument is completely microprocessor-controlled, for signal processing and automatic laser stabilization. The goal for instrument sensitivity is 5 ppb methane (0.3% of ambient), with a cell flushing time of 3 seconds.

SUMMARY OF PROGRESS AND RESULTS :

Aerodyne Research has successfully completed the development of the core of an infrared laser-based atmospheric methane instrument, which with further development should be suitable for deployment on the NASA ER-2 aircraft. The measurement of methane in the stratosphere is important because methane is, through photochemical processes, the main source of water vapor and hydroxyl radicals in the stratosphere. Thus it plays important roles in the chemical cycles of the upper atmosphere, including the cycles leading to ozone depletion. We have constructed and tested a methane measurement instrument which includes the following subsystems: a magnetically-broadened infrared HeNe laser, laser control and signal processing electronics, an optical system with a low pressure, fast response multipass absorption cell, and a gas handling system for bench testing. A flight qualified instrument will require a more robust mechanical structure and enclosure, a more complete gas sampling system, an enlarged data processing and control system, and extensive pre-flight testing.

Tests to date indicate that we have met our goals for the basic instrument performance. The current minimum detectable level of change in methane concentration is 5 ppb (RMS noise, one second time constant), out of an ambient concentration of 1680 ppb. The baseline drift has been demonstrated as low as 15 ppb (peak to peak) over 5 hours. The instrument automatically locks onto the laser line at turnon, controls the laser intensity and records methane measurements, all without operator intervention, which is essential for the ER-2 mission. The existing control system can

be expanded, using the same computer (Harris RTX 2000), to allow automatic calibration cycles, as well as logging of methane concentration and housekeeping data.

At the heart of the Aerodyne Stratospheric Methane Monitor is a unique infrared HeNe laser, which was invented at Aerodyne Research. This laser acts as an amplitude and frequency controlled light source that can be tuned on and off the center of a methane absorption line (near 2947 wavenumbers). This laser offers advantages in terms of reliability, weight and power consumption over tunable diode-lasers as a source for optical absorption measurements of methane. The ability to tune this gas laser over a range of .015 wavenumbers, with nearly uniform output, is derived from the application of a non-uniform transverse magnetic field to the laser plasma. The laser frequency is scanned over the methane line twenty times per second, while the output power is held constant to within one part in $\sim 10,000$. This allows us to detect the small fluctuations in transmission through an optical absorption cell that are caused by changes in atmospheric methane concentration. The laser output is actively controlled to compensate for ambient levels of methane by means of a column matching reference cell. Once calibrated, the system automatically detects deviations from the ambient methane level.

The methane monitor employs a fast flow response multipass optical absorption cell of the off-axis resonator (Herriott cell) design. With an effective gas volume of 1.5 liters, we obtain an optical absorption length of over 50 meters, which gives an absorption due to ambient methane at 40 Torr pressure of $\sim 10\%$. The optical train also includes a column matching reference cell for laser amplitude control, and a high concentration methane cell for laser line locking.

JOURNAL PUBLICATIONS:

We plan to publish a description of this work at a later time. We have written a paper describing a related laser-based methane instrument, which was developed for the NASA-ABLE3A experiment. That paper is scheduled to appear in Applied Optics on December 1, 1989.

II. LABORATORY STUDIES

A. KINETICS AND PHOTOCHEMISTRY

B. SPECTROSCOPY

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A. KINETICS AND PHOTOCHEMISTRY

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UPPER ATMOSPHERE RESEARCH: REACTION RATE AND OPTICAL MEASUREMENTS

Principal Investigators: L. J. Stief and J. E. Allen, Jr.

Co-Investigators: D. F. Nava and W. A. Payne, Jr.

Code 691, Goddard Space Flight Center, Greenbelt, MD 20771

Abstract of Research Objectives

The objective of this research program is to provide photochemical, kinetic and spectroscopic information necessary for photochemical models of the Earth's upper atmosphere and to examine reactions or reactants not presently in the models to either confirm the correctness of their exclusion or provide evidence to justify future inclusion in the models. New initiatives are being taken in technique development (many of them laser based) and in the application of established techniques to address gaps in the photochemical/kinetic data base, as well as to provide increasingly reliable information.

SUMMARY OF PROGRESS AND RESULTS

1. Reaction Rates and Reaction Products

The reactions of the hydroxymethyl radical with O_2 , NO and NO_2 have been studied in a discharge flow system as a function of temperature; formaldehyde (H_2CO) was identified as a product for all three reactions. The results at 298 K for O_2 , NO and NO_2 respectively are: $k_1 = 8.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $k_2 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $k_3 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The rate constants at mid stratospheric temperatures (220 K) are 2 to 3 times lower than at 298 K. A chemical link between natural and anthropogenic bromine species and ozone depletion in the Arctic atmosphere has recently been suggested. We have now examined the reaction $Br + C_2H_4$ and the result obtained was $k_4 = 1.6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ independent of temperature (268-423 K) and total pressure (15-400 Torr Argon). In the presence of up to 2 Torr O_2 , k_4 increased by an order of magnitude. At a fixed O_2 concentration (0.75 Torr), k_4 increased by a factor of 3 when total pressure was increased from 10 to 800 Torr Argon.

We have initiated a temperature study of the reaction of Cl with CH_3CHO , an intermediate in the atmospheric oxidation of C_2 hydrocarbons. The reactions of Cl with oxygenated hydrocarbons have generally not been as well studied as those with the hydrocarbons themselves. The results obtained were k_5 (298 K) = $6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and k_5 (210 K) = $7.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Work is in progress at $T > 298 \text{ K}$. This is the first direct and absolute study of this reaction but it is consistent with previous indirect and/or relative studies at 298 K.

Collaborative work was also performed with Prof. D. Gutman (then at Illinois Institute of Technology) on the reaction $Br + i-C_4H_{10} \rightleftharpoons HBr + t-C_4H_9$ in both directions to obtain thermochemical properties such as the heat of formation for hydrocarbon free radicals. Also, collaboration with Dr. T. Wallington (Ford Research Division) on the pressure dependence of the reaction of Cl with C_2H_2 and C_2H_4 showed good agreement with our previous direct results on $Cl + C_2H_2$ but the more extensive pressure range of the new data leads to a larger value for k_{∞} at 298 K ($2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$).

Finally, we replaced the data collection and analysis system for the flash photolysis apparatus, the discharge flow system was modified to include photoionization detection, and our move to a new laboratory was completed.

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2. Optical and Spectroscopic Measurements

For the past several years we have conducted an experimental program to develop intracavity laser absorption spectroscopy for application to chemical problems related to stratospheric research. For NO_2 the absorption linewidth is narrower than the laser bandwidth and the technique gives quantitative results, if the data are represented by a modified Beer's law that is based on a measure of the apparent absorbance. Enhancements as high as 23,000 over conventional absorption were obtained. The same apparatus was then used to demonstrate the utility of the technique by measuring the rate for the reaction of NO with O_2 and the result was in excellent agreement with the recommended value.

Another study examined the case for which the absorption linewidth is broader than the laser bandwidth. Ozone (O_3) was used as the absorber and the experiments performed at 630 nm, corresponding to absorption in the Chappuis bands. It was determined that the absorption was best represented by absorptance ($\Delta I/I_0$) and followed a modified Beer's law. Enhancements in the range 10^2 to 10^3 were obtained, because mode competition does not play a role here. Thus, we determined that mode competition accounts for a factor of 10 to 10^2 in the enhancement for the narrowband case.

In the next phase O_3 was dissociated at 254 nm, producing O atoms with a quantum yield near unity. Intracavity absorption at 630 nm, corresponding to the $^1\text{D} \leftarrow ^3\text{P}$ transition, was clearly evident. $\text{O}(^3\text{P})$ atoms were directly and $\text{O}(^1\text{D})$ atoms in-directly detected in this system. This represents the first detection by intracavity laser absorption of O atoms produced by photolysis.

To investigate the utility of quasi-cw operation for application to time resolved experiments, a new experimental arrangement was implemented. This set up was used to measure weak absorption of combination bands in water vapor present as humidity in the room air. The absorbance was found to vary linearly with generation time for $t \leq 170 \mu\text{sec}$. This study indicates that this method can be used effectively to follow fast reactions of radicals.

Significant improvements have been made in both our facilities and the experiment. Our entire laboratory was moved to a recently completed laboratory wing that was specifically designed for our use. The intracavity dye laser absorption spectrometer has been significantly upgraded with the incorporation of a 1.26 m microprocessor-controlled spectrometer. An electro-optic modulator has been incorporated into the system for quasi-cw operation.

JOURNAL PUBLICATIONS

"Temperature Dependence for the Absolute Rate Constant for the Reaction $\text{CH}_2\text{OH} + \text{O}_2 \longrightarrow \text{HO}_2 + \text{H}_2\text{CO}$ from 215 to 300 K," F. L. Nesbitt, W. A. Payne and L. J. Stief, *J. Phys. Chem.*, **92**, 4030 (1988).

"Kinetics and Thermochemistry of the $t\text{-C}_4\text{H}_9$ Radical. Study of the Equilibrium $t\text{-C}_4\text{H}_9 + \text{HBr} \rightleftharpoons i\text{-C}_4\text{H}_9 + \text{Br}$," J. J. Russell, J. A. Seetula, R. S. Timonen, D. Gutman and D. F. Nava, *J. Amer. Chem. Soc.*, **110**, 3084 (1988).

"Kinetic Studies of the Reaction of the Hydroxymethyl Radical with NO and NO_2 ," F. L. Nesbitt, W. A. Payne and L. J. Stief, *J. Phys. Chem.*, **93**, 5158 (1989).

"Rate Determination for the Reaction $\text{NO} + \text{NO} + \text{O}_2$ Using Intracavity Dye Laser Absorption Spectroscopy," W. D. Brobst and J. E. Allen, Jr., submitted to *Int. J. Chem. Kin.*, (1989).

"Intracavity Dye Laser Absorption Spectroscopy with a Broadband Absorber: Detection of O_3 in the Chappuis Bands," W. D. Brobst and J. E. Allen, Jr., submitted to *Appl. Opt.*, (1989).

CHEMICAL KINETICS OF THE UPPER ATMOSPHERE

W. B. DeMore, L. F. Keyser, and M. T. Leu
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Objectives

To obtain direct measurements of rate constants and temperature dependences for reactions of HO_x , NO_x , ClO_x , BrO_x , and RO_x which are relevant to stratospheric chemistry, including both homogeneous and heterogeneous reactions on particle surfaces which are important in both the polar and normal stratospheric regions.

Progress

Measurements were made of the sticking coefficients of HCl , H_2O , HNO_3 , NO , NO_2 , and O_3 on ice surfaces. These measurements were accomplished by a flow reactor combined with mass spectral detection (FR/MS). Measurements were made of the reaction probabilities of $\text{ClONO}_2 + \text{HCl}$ and $\text{ClONO}_2 + \text{H}_2\text{O}$ reactions on ice surfaces by the FR/MS technique. The reaction probabilities of $\text{N}_2\text{O}_5 + \text{HCl}$ and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ on ice surfaces were measured by the FR/MS technique. The solubility of HCl in acid ices was measured by a diode laser/mass spectral method. Temperature dependence of the $\text{OH} + \text{HO}_2$ reaction was measured by the discharge flow/resonance fluorescence method.

Publications

1. "Kinetics of the Reaction $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ from 254 to 382K", L. F. Keyser, J. Phys. Chem. 92, 1193, (1988).
2. "Laboratory Studies of Heterogeneous Reactions and Thermodynamic Properties of Acid-Ice Surfaces Important in the Polar Stratosphere", L. F. Keyser, S. B. Moore, and M. T. Leu, 18th Informal Conference on Photochemistry, 1989.
3. "Laboratory Studies of Sticking Coefficients and Heterogeneous Reactions Important in the Antarctic Stratosphere", M. T. Leu, Geophys. Res. Lett. 15, 17 (1988).
4. "Heterogeneous Reactions of N_2O_5 with HCl and H_2O on Ice Surfaces: Implications for Antarctic Ozone Depletion", M. T. Leu, Geophys. Res. Lett. 15, 851, (1988).
5. "Rate Constants for Reactions between Atmospheric Reservoir Species II. H_2O ", S. Hatakeyama and M. T. Leu, J. Phys. Chem., in press, 1989.
6. "Rate Constants for Reactions between Atmospheric Species I. HCl ", M. T. Leu, S. Hatakeyama, and K. Y. Hsu, J. Phys. Chem., in press (1989).

LABORATORY INVESTIGATIONS OF STRATOSPHERIC BROMINE CHEMISTRY

Principal Investigator: Paul H. Wine

Collaborators: J. Michael Nicovich, Edward P. Daykin, R. Peyton Thorn, Mian Chin, Christie J. Shackelford, and Kevin D. Kruetter

Institution: Molecular Sciences Branch, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332

Research Objectives

The initial objectives of this task were to employ state-of-the-art experimental methods to investigate the kinetics of a number of reactions of the active bromine species Br and BrO which are of proven or potential importance in stratospheric chemistry, and to investigate the photochemistry of the important bromine reservoir species BrONO₂ (bromine nitrate). Subsequently, we expanded our objectives to include studies of the kinetics and thermochemistry of several weakly bound chlorine-containing species which may play a role in stratospheric ClO_x chemistry.

Progress and Results

Reactions studied during 1988 and 1989 are listed below along with a summary of results and a few pertinent comments.

- (1) $\text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2$
T dependence of k_1 , 195-392K; Good agreement with previous studies.
- (2) $\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$
T dependence of k_2 , 189-385K; Non-Arrhenius behavior observed; k_2 faster than previously thought at low T.
- (3) $\text{Cl} + \text{O}_2 + \text{O}_2 \rightleftharpoons \text{ClOO} + \text{O}_2$
 k_3 , k_{-3} , K_{eq} determined at T = 185K, P = 15-40 Torr; Third law method used to obtain ClOO heat of formation; k_3 faster than previously thought; ClOO less stable than previously thought.
- (4) $\text{Cl} + \text{CO} + \text{M} \rightleftharpoons \text{ClCO} + \text{M}$, M = N₂, CO, Ar, CO₂
T & P dependence of k_4 , k_{-4} , K_{eq} , 185-260K; Second and third law methods used to obtain ClCO heat of formation; ClCO more stable than previously thought.
- (5) $\text{Cl} + \text{CS}_2 + \text{M} \rightleftharpoons \text{CS}_2\text{Cl} + \text{M}$, M = N₂, O₂
T & P dependence of k_5 , k_{-5} , K_{eq} , 193-258K; Second law method used to obtain CS₂Cl heat of formation; CS₂Cl found to be unreactive toward O₂.
- (6) $\text{Cl} + \text{COS} + \text{N}_2 \rightleftharpoons \text{COSCl} + \text{N}_2$
Evidence of equilibrium between Cl and COSCl sought at low T (190K); No reaction observed.
- (7) $\text{Br} + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CO} + \text{HBr}$
First study T dependence of k_1 , 255-400K; k_7 (298K) found to be 25% faster than previously thought; 298K rate coefficient for CH₃CO + Br₂ → CH₃CBro + Br also determined.

- (8) $O + Br_2 \longrightarrow BrO + Br$
 k_8 independent of T, 255-350K, 40% faster than previously thought.
- (9) $O + HBr \longrightarrow OH + Br$
 T dependence of k_9 , 250-402K; Good agreement with previous studies;
 Confirmation of theoretically predicted non-Arrhenius behavior.
- (10) $Cl + Br_2 \longrightarrow BrCl + Br$
 k_{10} nearly gas kinetic, virtually independent of T, 298-401K.
- (11) $Cl + HBr \longrightarrow HCl + Br$
 T-dependence of k_{11} , 257-414K; Poor agreement with previous studies.
- (12) $Br + NO_2 + M \rightleftharpoons BrNO_2 + M$, $M = He, Ar, H_2, N_2, CO_2, CF_4$
 T- and P-dependence of irreversible association reaction, 259-346K,
 12.5-700 Torr; $BrNO_2$ dissociation observed at $T > 350K$ allowing
 determination of $BrNO_2$ heat of formation; Fall-off parameters
 determined; First T-dependence study and first study to investigate
 fall-off regime.
- (13) $BrO + NO_2 + N_2 \longrightarrow BrONO_2 + N_2$
 T- and P-dependence, 245-346K, 16-800 Torr; Good agreement with previous
 study at 298K; T-dependence of fall-off parameters determined.
- (14) $BrONO_2 + h\nu \longrightarrow \text{products}$
 Study initiated during summer of 1989.

Journal Publications

- "Temperature-Dependent Absorption Cross Sections for Hydrogen Peroxide Vapor," J. M. Nicovich and P. H. Wine, J. Geophys. Res. 93, 2417 (1988).
- "Kinetics of the Reactions of $F(^2P)$ and $Cl(^2P)$ with HNO_3 ," P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. 92, 2223 (1988).
- "Pulsed Laser Photolysis Kinetics Study of the $O(^3P) + ClO$ Reaction," J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. 89, 5670 (1988).
- "Kinetics of the $Br_2 - CH_3CHO$ Photochemical Chain Reaction," J. M. Nicovich, C. J. Shackelford and P. H. Wine, J. Photochem. Photobiol., A:Chem., submitted, March 1989.
- "Kinetics of Reversible Adduct Formation in the Reactions of $Cl(^2P_J)$ with CS_2 and COS ," J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Phys. Chem., submitted, May, 1989.
- "Kinetics of the Reactions of $Cl(^2P_J)$ and $Br(^2P_{3/2})$ with O_3 ," J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet., submitted, June, 1989.
- "Kinetics of the Reactions of $O(^3P)$ and $Cl(^2P)$ with HBr and Br_2 ," J. M. Nicovich and P. H. Wine, Int. J. Chem. Kinet., submitted, July, 1989.
- "Formation-Dissociation Kinetics and Thermochemistry of the $ClCO$ Radical," J. M. Nicovich, K. D. Kreutter, and P. H. Wine, manuscript in preparation for submission to J. Phys. Chem., Second International Conference on Chemical Kinetics special issue, September, 1989.

A MOLECULAR BEAM MASS SPECTROMETRIC STUDY OF THE FORMATION AND PHOTOLYSIS OF C10 DIMER

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Research Objectives

The dimer of C10 radical has been proposed as a key intermediate in the catalytic destruction of ozone in the antarctic stratosphere. To date evidence for the existence of this transient species has come from infrared and ultraviolet spectroscopic observations in laboratory studies. The objectives of this research program are the identification of C10 dimer by molecular beam mass spectrometry, the measurement of the rate of formation of the dimer over a wide range of temperatures and pressures, and the elucidation of the photochemistry of the dimer.

Summary of Progress and Results

The objective of the first phase of this work was the determination of whether the C10 dimer could be measured mass spectrometrically in preparation for studies of its kinetic and photochemical behavior. In this work the dimer of C10 was generated in four different chemical systems by the combination of C10 radicals in a simple flow reactor operated at total pressures ranging from 5 to 200 torr, temperatures from -40° to 20°C and residence times from 0.04 to 2 sec. The C10 radicals were produced by the reaction of Cl atoms, which were generated by photolysis of Cl₂ with C10₂, O₂, or Cl₂O and by the reaction of thermally generated Cl atoms with C10₂. The flow reactor was interfaced to a molecular beam mass spectrometric system which incorporated both a large magnetic mass spectrometer with high resolution capabilities and a quadrupole mass spectrometer, and which utilized beam modulation and phase sensitive detection. This system, which was optimized for operation at pressures up to 1 atm and which had a detection limit of better than 1 ppb, was used to obtain mass spectra of the reaction products at an ionizing energy of 20 eV. In addition to the expected signals for reactants and C10 radicals, strong signals were also obtained at m/e = 102, 104 and 106. These ions were assigned to the dimer of C10 based on: (1) The mass to charge ratio, (2) the excellent agreement between the observed and calculated isotope ratios, (3) the fact that the ions were only observed in the presence of light in the photolysis experiments or when the furnace temperature was great enough to dissociate Cl₂ in the thermal experiments, and (4) the weak dependence of the ratio of C10 dimer to C10 on reactor pressure, which suggested that it was not being produced in the initial beam forming process during sampling.

The mass spectrometric identification of the ClO dimer was further supported by time-of-flight velocity analyses. Velocity distributions were obtained for the neutral precursors of the dimer of ClO and for several other species. These distributions showed that the neutral precursor of Cl_2O_2^+ has a nominal mass of 102 amu and that Cl_2O_2^+ cannot be a fragment from a significantly larger molecule, such as one containing one or more additional chlorine or oxygen atoms.

The results obtained to date show that ClO dimer can be readily measured by molecular beam mass spectrometry. It should therefore be possible to utilize this technique to make detailed measurements of the kinetics of formation and photochemical behavior of the dimer.

LABORATORY STUDIES OF HETEROGENEOUS PROCESSES IN THE ATMOSPHERE

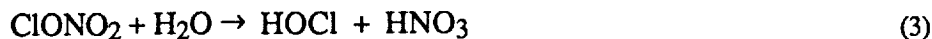
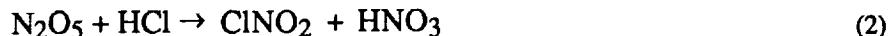
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RESEARCH OBJECTIVES

Heterogeneous reactions on the surfaces of polar stratospheric clouds (PSCs) are now recognized to play a central role in the dramatic yearly occurrence of the Antarctic 'ozone hole'. In addition, heterogeneous reactions on normal stratospheric particulate may be important in the global ozone cycle. The goal of this research program is to identify and quantify heterogeneous processes that may have an impact on the stratospheric ozone layer. The surfaces of interest for stratospheric chemistry include ice, concentrated frozen mixtures of nitric acid and ice, and concentrated liquid solutions of sulfuric acid and water.

SUMMARY OF PROGRESS AND RESULTS

Heterogeneous interactions on model PSC surfaces. A Knudsen cell flow reactor was used to study the heterogeneous reactions (1-4) of chlorine nitrate (ClONO_2) and



dinitrogen pentoxide (N_2O_5) on ice surfaces representative of type II PSCs. All four reactions occurred readily on laboratory ice surfaces at 185 K. Reactions 1,2 and 3 formed gaseous products Cl_2 , ClNO_2 and HOCl , respectively. All of these molecules could be readily photolyzed in the Antarctic spring sunlight to form active chlorine for catalytic ozone destruction cycles. Surface evaporation studies showed that reactions 1-4 all resulted in the formation of HNO_3 condensed in the ice. Nitric acid condensed in PSCs

would provide a sink for odd nitrogen during the polar winter, a requirement in nearly all models of Antarctic ozone depletion.

Heterogeneous processes on sulfuric acid surfaces. The heterogeneous interactions of ClONO_2 , HCl and HNO_3 were studied on sulfuric acid surfaces representative of global stratospheric particulate. The surfaces were composed of 65-75% sulfuric acid and were held at temperatures in the range 210 to 230 K. Heterogeneous loss, but not reaction, of HNO_3 and HCl occurred on these surfaces. Chlorine nitrate reacted on the cold sulfuric acid surfaces, producing gas phase HOCl . Nitric acid was formed partitioned between the gas and condensed phases. Chlorine nitrate also reacted with HCl dissolved in the more dilute sulfuric acid solutions, forming gaseous Cl_2 . In all cases studied, the sticking and/or reactions coefficients were much larger for the more dilute sulfuric acid solutions.

JOURNAL PUBLICATIONS

1. "Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures", M.A. Tolbert, M.J. Rossi, R. Malhotra and D.M. Golden, *Science* 238, 1258-1260, 1987.
2. "Antarctic ozone depletion chemistry: reactions of N_2O_5 with H_2O and HCl on Ice Surfaces", M.A. Tolbert, M.J. Rossi and D.M. Golden, *Science* 240, 1018-1021, 1988.
3. "Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surfaces at stratospheric temperatures", M.A. Tolbert, M.J. Rossi and D.M. Golden, *Geophys. Res. Lett.* 15, 847-850, 1988.

PHOTOCHEMICAL AND KINETIC MEASUREMENTS OF ATMOSPHERIC CONSTITUENTS VIS-A-VIS THEIR ROLE IN CONTROLLING STRATOSPHERIC OZONE

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Collaborators: Philippe Dagaut, Robert E. Huie, Renzhang Liu, and
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Research Objectives

This task focuses on the elucidation of stratospheric photochemical kinetics through laboratory studies of select chemical reaction systems. Experiments are designed and conducted to determine the temperature and pressure dependencies of rate constants and to infer the mechanisms for those processes important in the modeling of atmospheric chemistry. While the research emphasis is directed towards an assessment of the effects of anthropogenic activity on stratospheric chemical composition, certain predominantly tropospheric reaction systems are also investigated because of their influence on chemical transport to the stratosphere and/or their mechanistic similarities to stratospheric processes. Under this task, the principal investigator also serves as a member of the NASA Panel for Data Evaluation and assists in the annual preparation of a tabulation of evaluated kinetic and photochemical data applicable to atmospheric modeling.

Summary of Progress and Results

Laboratory activities under this task during 1988 and 1989 fall into two general experimental categories: a) peroxy radical studies conducted via flash photolysis uv absorption spectroscopy (FPAS) and b) hydroxyl radical kinetic investigations performed using the flash photolysis resonance fluorescence (FPRF) technique. Accomplishments under both categories include:

FPAS: UV Absorption Cross-Sections for CH_3O_2 , CH_2ClO_2 , CH_2FO_2 , $\text{CH}_2\text{ClCH}_2\text{O}_2$, $\text{CH}_3\text{OCH}_2\text{O}_2$, and $\text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2$.

$\text{CH}_2\text{ClO}_2 + \text{CH}_2\text{ClO}_2$ Kinetics - Temperature dependence of the rate constant.

$\text{CH}_2\text{FO}_2 + \text{CH}_2\text{FO}_2$ Kinetics - Temperature dependence of the rate constant.

$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{CH}_2\text{ClCH}_2\text{O}_2$ Kinetics - Temperature dependence of the rate constant.

$\text{CH}_3\text{OCH}_2\text{O}_2 + \text{CH}_3\text{OCH}_2\text{O}_2$ Kinetics - Temperature and pressure dependence of the rate constant.

$\text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2 + \text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2$ Kinetics - Temperature and pressure dependence of the rate constant.

CF₂ClO₂ + Cl Reaction - Modeling estimate of the rate constant at room temperature.

FPRF: OH Reaction Kinetics - Temperature dependencies of the rate constants for the reactions with alcohol and ether fuel additives, carboxylic acids, C₅ through C₇ aliphatic alcohols and ethers, cyclic ketones and diones, difunctional organic oxygenates, cyclic ethers, aliphatic polyethers, and chlorofluoroethanes.

Journal Publications

1. "The Gas Phase Reactions of Hydroxyl Radicals with the Fuel Additives Methyl-t-Butyl Ether and t-Butyl Alcohol over the Temperature Range 240 - 440 K", T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Environ. Sci. and Tech.* **22**, 842 (1988).
2. "The Gas Phase Reactions of Hydroxyl Radicals with a Series of Carboxylic Acids over the Temperature Range 240 - 440 K", P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988).
3. "Rate Constants for the Gas Phase Reaction of OH Radicals with C₅ through C₇ Aliphatic Alcohols and Ethers: Predicted and Experimental Values", T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.*, **20**, 541 (1988).
4. "A Kinetics Investigation of the Gas Phase Reaction of OH Radicals with Cyclic Ketones and Diones: Mechanistic Insights", P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *J. Phys. Chem.*, **92**, 4375 (1988).
5. "A Correlation Between Gas Phase and Solution Phase Reactivities of OH Radicals towards Saturated Organic Compounds", T. J. Wallington, P. Dagaut, and M. J. Kurylo, *J. Phys. Chem.* **92**, 5024 (1988).
6. "The UV Absorption Spectra and Kinetics of the Self Reactions of CH₂ClO₂ and CH₂FO₂ Radicals in the Gas Phase", P. Dagaut, T. J. Wallington, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 815 (1988).
7. "A Flash Photolysis Kinetic Spectroscopy Investigation of the Absorption Spectrum and Self-Reaction of C₂H₄ClO₂ Radicals in the Gas Phase", *Chem. Phys. Lett.* **146**, 589 (1988).
8. "Group Reactivities in the Gas Phase Reactions of Hydroxyl Radicals with Ethers", *Acta Physico-Chimica Sinica* **5**, 210 (1989).
9. "Gas Phase Studies of Substituted Methyl Peroxy Radicals: The UV Absorption Spectrum and Self-Reaction Kinetics of CH₃OCH₂O₂; The Reaction of CF₂ClO₂ with Cl Atoms", P. Dagaut, T. J. Wallington, and M. J. Kurylo, *J. Photochem. and Photobiol., A: Chem.* **48**, 187 (1989).
10. "Kinetic Measurements of the Gas Phase Reactions of OH Radicals with Hydroxyethers, Hydroxyketones, and Ketoethers", P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.*, **93**, xxxx (1989).

11. "The Gas Phase Reactivity of Aliphatic Polyethers towards OH Radicals: Measurements and Predictions", P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *Int. J. Chem. Kinet.* **21**, xxxx (1989).
12. "A Flash Photolysis Resonance Fluorescence Investigation of the Gas Phase Reactions of Hydroxyl Radicals with a Series of Cyclic Ethers", P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.*, in press (1989).
13. "The UV Absorption Spectra of Methylperoxy Radicals in the Gas Phase: A Reinvestigation", P. Dagaut and M. J. Kurylo, *J. Photochem. and Photobiol., A: Chem.*, in press (1989).
14. "A Flash Photolysis Investigation of the Gas Phase UV Absorption Spectrum and Self-Reaction Kinetics of the Neopentylperoxy Radical", *Int. J. Chem. Kinet.*, submitted for publication (1989).
15. "An Evaluation of the Gas Phase Reaction Rates of OH Radicals and O(¹D) Atoms with Select Chlorofluorocarbons and Fluorocarbons", prepared for the Alternate Fluorocarbon Environmental Acceptability Study (AFEAS), UNEP/WMO Special Report (1989).
16. "A Flash Photolysis Resonance Fluorescence Investigation of the Reactions of OH Radicals with Chlorofluoroethanes", R. Liu, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.*, submitted for publication (1989).

Biennial Report for NASA

SPECTROSCOPIC STUDIES OF REACTION INTERMEDIATES AND PRODUCTS

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Research Objectives

This project involves spectroscopic studies of reaction rates, intermediates and products. A high resolution Fourier transform spectrometer and a linear photodiode array spectrometer are used to obtain IR, visible, and UV spectra of transient and stable species of atmospheric importance. Reaction rate constants are measured, reaction mechanisms are analyzed, and spectra and absorption cross sections are determined for stable and labile chemical species. The results obtained help reduce some of the uncertainties in stratospheric chemistry and provide spectroscopic data for laboratory and field measurements.

Progress and Results

1) Antarctic Ozone Hole Chemistry

(a) The ultraviolet and infrared absorption cross sections of Cl_2O_2 were measured by producing it via the reaction, $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$. The ClO radical was produced by: $\text{Cl} + \text{O}_3$, $\text{Cl} + \text{Cl}_2\text{O}$, or $\text{Cl} + \text{OCIO}$ reaction. The UV absorption spectrum between 205 and 250 K was recorded over the 200 - 450 nm range with a diode array spectrometer. The infrared spectrum was recorded with a high resolution Fourier transform spectrometer. Both spectrometers were optically coupled to a fast flow multipass absorption cell to permit simultaneous IR and UV measurements on the same gas sample. The UV absorption spectrum of Cl_2O_2 is a structureless continuum with a maxima at 245 nm and a long wavelength tail which extends out to 410 nm. The UV absorption cross section at 245 nm was measured to be $(6.5 \pm 1.0) \times 10^{-18} \text{ cm}^2$. Infrared absorption features centered at 570, 653, and 750 cm^{-1} were assigned to the Cl_2O_2 molecule. The UV spectrum of Cl_2O_2 allows the calculation of its photolytic lifetime in the atmosphere.

(b) The rate coefficient for the reaction which forms Cl_2O_2 , $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$, was measured between 200 and 265 K in the pressure range of 25 to 600 Torr of He, N_2 , O_2 and SF_6 . The loss of ClO was monitored via UV absorption at 282.7 nm (9-0 band) using a monochromator or via UV absorption between 270 and 300 nm using a spectrometer/diode array system. The measured rate coefficients are lower than those published earlier and were carried out at or near Antarctic temperatures. Using this data more accurate ozone depletion calculations can be carried out.

(c) The UV absorption cross sections of ClO in the $\text{A}^2\Pi \leftarrow \text{x}^2\Pi$, system (225 to 325 nm) were measured as a function of temperature between 200 and 300 K. The cross section at the top of the continuum, 265 nm, was measured to be $(5.33 \pm 0.50) \times 10^{-18} \text{ cm}^2$, independent of temperature. The cross sections in the structured part, 270 - 300 nm, are very temperature and instrumental resolution dependent. These measurements provide necessary data for field and laboratory measurements of ClO .

2) High Resolution IR Spectroscopy

(a) IR Line positions of HNO_3

High resolution measurements were made on the ν_9 band of HNO_3 from 414 to 500 cm^{-1} . Over 2300 transitions were measured, assigned, and fit to obtain 15 rovibrational constants for the $\nu_9 = 1$ state that reproduce the observed spectrum with a RMS deviation of 0.0004 cm^{-1} . The band center for ν_9 is at $458.2287 \pm 0.0005 \text{ cm}^{-1}$. These measurements provide data necessary to interpret atmospheric IR measurements of the ν_9 band of HNO_3 .

(b) Fundamental IR intensities of ClO

The fundamental, $v = 0 - 1$, vibrational band intensity of the ClO radical was measured using a high resolution Fourier transform spectrometer (FTS) with calibrated flows of ClO. A source of systematic error in the use of the $\text{Cl} + \text{O}_3$ reaction as a stoichiometric source of ClO was discovered. Our result on the band intensity is in general agreement with all other recent measurements except one.

Journal Publications:

High-Resolution Infrared Fourier Transform Spectroscopy of SO in the $X^3\Sigma$ and $a^1\Delta$ Electronic States, James B. Burkholder, Edward R. Lovejoy, Philip D. Hammer, Carleton J. Howard, and Masataka Mizushima, *J. Molecular Spectroscopy* **124**, 379 - 392, 1987.

High Resolution Fourier Transform Infrared Spectra of $^{12}\text{C}^{32}\text{S}$, $^{12}\text{C}^{33}\text{S}$, $^{12}\text{C}^{34}\text{S}$, and $^{13}\text{C}^{32}\text{S}$, James B. Burkholder, Edward R. Lovejoy, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy* **124**, 450 - 457, 1987.

Fourier Transform Infrared Spectra of the FO_2 Radical, A.R.W. McKellar, James B. Burkholder, Amitabha Sinha, and Carleton J. Howard, *J. Molecular Spectroscopy* **125**, 288 - 308, 1987.

High-Resolution Fourier Transform Infrared Spectroscopy of the Fundamental Bands of HNC, James B. Burkholder, Amitabha Sinha, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy* **126**, 72 - 77, 1987.

Fourier Transform Spectroscopy of the ν_1 and ν_3 Fundamental Bands of CF_2 , James B. Burkholder, Carleton J. Howard, and Peter A. Hamilton, *J. Molecular Spectroscopy* **127**, 362 - 369, 1988.

Fourier Transform Infrared Spectrum of the ν_2 Band of the NH_2 Radical, James B. Burkholder, Carleton J. Howard, and A.R.W. McKellar, *J. Molecular Spectroscopy* **127**, 415 - 424, 1988.

High-Resolution Fourier Transform Infrared Spectroscopy of the CCl Radical ($X^2\Pi_{3/2,1/2}$), James B. Burkholder, Amitabha Sinha, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy* **127**, 61 - 69, 1988.

Fourier Transform Infrared Spectroscopy of the BO_2 Radical, Arthur G. Maki, James B. Burkholder, Amitabha Sinha, and Carleton J. Howard, *J. Molecular Spectroscopy* **130**, 238 - 248, 1988.

High Resolution Study of FO Infrared Chemiluminescence, Philip D. Hammer, Amitabha Sinha, James B. Burkholder, and Carleton J. Howard, *J. Molecular Spectroscopy*, **129**, 99 - 118, 1988.

Spectroscopic Constants for the ν_9 Infrared Band of HNO_3 , Aaron Goldman, James B. Burkholder, and Carleton J. Howard, *J. Molecular Spectroscopy*, **131**, 195 - 200, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the N_3 Radical, Chris Brazier, Peter Bernath, James B. Burkholder, and Carleton J. Howard, *J. Chemical Physics*, **89**, 1762 - 1767, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the NS Radical, Amitabha Sinha, James B. Burkholder, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy*, **130**, 466 - 469, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the HCO Radical, A.R.W. McKellar, James B. Burkholder, John Orlando, and Carleton J. Howard, *J. Molecular Spectroscopy*, **130**, 445 - 453, 1988.

Absorption Cross Sections of BrO between 312 and 385 nm at 298 and 223 K, A. Wahner, A.R. Ravishankara, S.P. Sander, and R.R. Friedl, *Chem. Phys. Lett.* **152**, 507 - 512, 1988

Infrared Line Strength Measurements of the ClO Radical, James B. Burkholder, Philip D. Hammer, Carleton J. Howard, and Aaron Goldman, *J. Geophysical Research*, **94**, D2, 2225 - 2234, 1989.

- A. Laboratory Measurements of Photolytic and Kinetic Data Affecting Atmospheric Ozone
- B. Tom G. Slanger, Molecular Physics Laboratory, SRI International, Menlo Park, CA.
- C. Research Objectives. The experimental part of the program has been directed towards an improved understanding of ozone photochemistry, as related to upper atmospheric issues. Apart from the well-publicized Antarctic ozone hole, there are other discrepancies that are found between what modelers predict for the ozone altitude profiles, and what is actually observed. At present, there is an excess amount of ozone in the upper stratosphere and lower mesosphere at temperate latitudes compared to modeling predictions, amounting to 50-100%. This is obviously a consequence of either an underestimation of sources, or an overestimation of losses. We have pursued the former hypotheses, and have shown that the role of vibrationally excited oxygen may be crucial in the photochemistry of the upper stratosphere.
- D. Progress and Results. The essence of the work carried out in 1988 has been to demonstrate that the atmosphere has an unexpected potential source of ozone which has not been included in current models. It has always been taken for granted that ozone itself cannot be an ozone source, and that it can only be generated by oxygen photodissociation.

We have shown in the laboratory that irradiation of a dilute mixture of ozone in oxygen with a KrF laser at 248 nm generates more ozone, contrary to the conventional chemistry which predicts that at this wavelength, all ozone will eventually be converted to oxygen. We have demonstrated that the reason that this occurs is that the generally ignored photodissociative channel in the Hartley band, that giving vibrationally excited oxygen and a ground state oxygen atom, is very important. Although only 10-15% of the dissociative process takes place by this pathway, as opposed to the major $O(^1D) + O_2(a^1\Delta_g)$ channel, the effect of the presence of highly vibrationally excited oxygen is to act as an ozone source.

In the laboratory, this occurs because there is a strong Schumann-Runge oxygen absorption band in the neighborhood of 248 nm. The transition is that between ground state oxygen in the $v=7$ vibrational level, and electronically excited $B^3\Sigma_u^-$ oxygen in the $v=2$ level. It turns out that ozone photodissociation at this wavelength generates a range of vibrational levels in oxygen, including $v=7$. Such molecules are excited by the same laser pulse to the $B(2)$ level, from where they dissociate, resulting in one molecule of ozone being fragmented by two photons (not necessarily delivered simultaneously) into three atoms of oxygen. These atoms then recombine into three ozone molecules, and the process is a self-catalyzed ozone amplifier.

In the atmosphere, the same process has an advantage in that the solar continuum can in principle pump all vibrational levels that are produced during ozone photodissociation. In order to evaluate the possible effectiveness of the process as a stratospheric ozone source, two types of measurements are necessary; the determination of the distribution of vibrationally excited oxygen produced from 200-300 nm photodissociation of ozone, and the rate at which these molecules are quenched, presumably by oxygen. These measurements are currently being carried out.

- E. Slanger, T. G., L. E. Jusinski, G. Black, and G. E. Gadd, A new laboratory source of ozone and its potential atmospheric implications, *Science*, 241, 945, 1988.

LABORATORY STUDIES OF TROPOSPHERIC AND STRATOSPHERIC REACTIONS

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Objectives

The primary objective of this task is to study the rates and mechanisms of key elementary gas-phase reactions important in stratospheric and tropospheric chemistry. A secondary objective is to utilize high-resolution spectroscopic techniques in the ultraviolet, infrared and microwave regions to determine structural parameters and measure line positions and strengths of atmospheric molecules.

Summary of Progress and Results

Considerable progress has been made in the last two years. Work has focused primarily on reactions important in polar stratospheric chemistry and the formation of the Antarctic ozone hole. The following studies in kinetics and spectroscopy were completed:

1. $\text{BrO} + \text{ClO} \rightarrow \text{Products}$. The reaction of ClO with BrO was investigated by two independent techniques, discharge flow-mass spectrometry and flash photolysis-UV absorption, over the temperature range 220-400 K and the pressure range 1-760 torr. Rate constants were determined for three product channels: a) $\text{Br} + \text{ClOO}$, b) $\text{Br} + \text{OClO}$ and c) $\text{BrCl} + \text{O}_2$. The results from the discharge flow and flash photolysis experiments were in good agreement and showed a significantly larger temperature dependence for the overall rate constant than previous work. In disagreement with previous studies, the channel forming BrCl was found to be significant (8%). The flash photolysis experiment also investigated the reaction, $\text{Br} + \text{Cl}_2\text{O} \rightarrow \text{BrCl} + \text{ClO}$, and the products of Cl_2O photolysis.
2. $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$. The gas-phase recombination of ClO has been investigated under the conditions of pressure and temperature that prevail in the Antarctic stratosphere during the period of maximum ozone disappearance. The temperature and pressure dependence of the rate constant fall-off behavior was determined using the flash photolysis-ultraviolet absorption technique. Fall-off parameters were derived for N_2 , O_2 and He bath gases. The measured rate constants were smaller than the previously accepted values by more than a factor of two. The results of the rate constant measurements were incorporated into a one-dimensional photochemical model to evaluate the relative rates of ozone depletion in the Antarctic stratosphere by the known catalytic cycles.
3. Molecular Structure of the ClO Dimer by Submillimeter Wave Spectroscopy. The products of the ClO self-reaction have been investigated between 220 K and 300 K by submillimeter wave spectroscopy. Chlorine peroxide, ClOOCl , has been definitively identified in the product mixtures. Below 240 K this species is found to be the predominant product. The complete spectrum between 415 and 435 GHz has been measured as well as selected transitions in the range 285 to 415 GHz. The rotational constants as well as a complete set of quartic centrifugal distortion constants have been determined. Structural parameters for the vibronic ground state have also been calculated.

4. Infrared Band Strength Measurement of the ClO Radical. High resolution (0.005 cm^{-1}) FTIR spectra of the $X^2\Pi_i-X^2\Pi_i$ (1-0) rovibrational bands of $^{35}\text{Cl}^{16}\text{O}$ and $^{37}\text{Cl}^{16}\text{O}$ have been obtained in 1 torr of helium carrier gas. After measuring the strengths of approximately 830 individual lines from several spectra, a total band strength, $S_V = 13.1 \pm 1.1\text{ cm}^{-2}\text{ atm}^{-1}$, and a first Herman-Wallis coefficient, $\alpha = (4.12 \pm 0.62) \times 10^{-3}$, were determined. The fundamental transition moment calculated from the band strength was $-(3.9 \pm 0.2) \times 10^{-2}\text{ D}$.

Journal Publications

1. Sander, S. P. and Friedl, R. R., "Kinetics and Mechanism of the BrO + ClO Reaction: Implications for Antarctic Ozone Depletion", *Geophys. Res. Lett.*, **15**, 887 (1988).
2. Lang, V. I., Sander, S. P. and Friedl, R. R., "Absolute Infrared Band Strength Measurement of the ClO Radical by FTIR Spectroscopy", *J. Mol. Spectrosc.*, **132**, 89 (1988).
3. Wahner, A., Ravishankara, A. R., Sander, S. P. and Friedl, R. R., "Absorption Cross Section of BrO Between 312 and 385 nm at 298 K and 225 K", *Chem. Phys. Lett.* **152**, 507 (1988).
4. Friedl, R. R. and Sander, S. P., "Kinetics and Product Studies of the Reaction ClO + BrO Using Discharge Flow-Mass Spectrometry", *J. Phys. Chem.*, **93**, 4756 (1989).
5. Sander, S. P. and Friedl, R. R., "Kinetics and Product Studies of the Reaction by Flash Photolysis-Ultraviolet Absorption", *J. Phys. Chem.*, **93**, 4764 (1989).
6. Anderson, J. G., Brune, W. H., Lloyd, S. A., Sander, S. P., Starr, W. L., Loewenstein, M. and Podolske, J. R., "Kinetics of O₃ Destruction by ClO and BrO Within the Antarctic Vortex: An Analysis Based on In Situ ER-2 Data", *J. Geophys. Res.*, in press.
7. Sander, S. P., Friedl, R. R. and Yung, Y. L., "Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss", *Science*, in press.
8. Birk, M., Friedl, R. R., Cohen, E. A., Pickett, H. M. and Sander, S. P., "The Rotational Spectrum and Structure of Chlorine Peroxide", *J. Chem. Phys.*, in press.

KINETICS AND MECHANISMS OF STRATOSPHERIC CHLORINE RELEASE FROM CHLOROFLUOROMETHYL SPECIES

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Research Objectives

The objective of this project is to conduct laboratory investigations leading to an understanding of the kinetics and mechanisms of Cl atom release from chlorofluorocarbons in the stratosphere. After the initial photolysis step, releasing the first Cl atom, peroxy radicals are formed rapidly by addition of O₂ to the chlorofluoromethyl photofragment. The ensuing reactions of the peroxy radical lead to photooxidation products that are formed by a complex and only partially understood mechanism. The work aims to reveal the steps in the mechanism and the pertinent kinetic parameters at stratospheric pressures and temperatures, and to assess the importance of these reactions with respect to inclusion in stratospheric models used for predicting O₃ depletion.

Summary of Progress and Results

The kinetics of the termolecular reaction of CF₂ClO₂ radicals with NO₂ was studied by flash photolysis of CF₂ClBr in the presence of O₂ and NO₂ by means of time resolved mass spectrometry. A quadrupole mass spectrometer fitted with a Daly detector for ion counting was employed to detect the decay rates of the peroxy radicals via the CF₂O₂ + (m/z =82) fragment ion. An investigation of this reaction over the pressure range 1 to 10 torr and the temperature range 248K to 325K has now been completed.

During the course of this work, the signal to noise ration was vastly improved by adding cryogenic pumping to the ion source region, and replacement of our homemade axial geometry ionizer with a cross beam ionizer.

To assist in the analysis of this complex reaction system, a computer code (LSODE) was used to perform numerical simulations on the U of M CDC CYBER 170-877 computer. The calculations were done primarily to identify possible important secondary reactions, to verify assumptions made in analysis of the experimental data, and to insure that the reaction of interest was, in fact, isolated.

The formation of peroxy nitrates by addition of halomethylperoxy radicals to NO_2 raises the question of the stratospheric stability of these species. We have built a continuous flow photoreactor for synthesis of halomethylperoxynitrates, and have been successful in obtaining pure samples of $\text{CF}_2\text{ClO}_2\text{NO}_2$. An investigation of its thermal decomposition is now underway, with an investigation of the photochemistry slated for the near future. The thermal decomposition studies are being done mass spectrometrically. A thermostatted batch reactor having a pinhole leak adjacent to the ion source permits decay of the reactant to be followed in real time.

Loss of reactant by flow through the pinhole should be corrected for. The flow is in the transition region, intermediate between bulk flow and Knudsen flow. Modeling this flow has proved difficult in the past, and our approach was to do empirical calibrations. During the course of the calibration work, we discovered that a simple interpolation formula gave a very accurate description of the net flow rates. Since this seems useful to others who use mass spectrometry for kinetics, we will publish the results.

Finally, in parallel with the experimental investigations, we redesigned the mass spectrometer sampling system, currently pinhole sampling, to a molecular beam sampling system. The machine shop work has been completed, and installation will be undertaken shortly.

Publications

228.8 nm Photolysis of 1,1,1-Trichloroethane. G-Y. Chung and R. W. Carr, J. Photochem., accepted.

Kinetics of the Reactions of CF_2ClO_2 Radicals with Nitrogen Dioxide. S. B. Moore and R. W. Carr, J. Phys. Chem., accepted.

Temperature Dependence of the Reaction of CF_2ClO_2 Radicals with NO_2 . F-S. Wu and R. W. Carr, to be submitted.

A Simple Interpolation Formula for Pinhole Flow in the Transition Regime. Q-J. Xiong and R. W. Carr, to be submitted.

LABORATORY STUDIES OF CHEMICAL AND PHOTOCHEMICAL PROCESSES RELEVANT TO STRATOSPHERIC OZONE

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RESEARCH OBJECTIVES

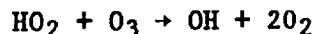
This program's purpose is to provide laboratory kinetic and thermodynamic data for stratospheric processes which will contribute to reducing the discrepancy between measurements and models in several areas: 1) HO_x chemistry including the reaction of HO_2 with ozone at stratospheric temperatures, 2) the isotopic ozone anomaly in the mid-stratosphere including the mechanisms for "heavy" ozone formation, 3) upper stratospheric sodium chemistry investigating the possible impact of meteoric sodium compounds on chlorine-catalyzed ozone destruction, 4) the thermochemistry of stratospheric aerosols including measurements of equilibrium vapor pressures and solubilities of HCl in aqueous nitric acid and sulfuric acid particles. The results of these studies will provide data both for modeling the chemistry of ozone depletion and for designing improved field measurements of stratospheric constituents.

SUMMARY OF PROGRESS AND RESULTS

HO_2 Spectroscopy and Chemistry

Infrared line intensities in the three fundamental vibrational bands of the HO_2 radical have been measured using a tunable diode laser coupled with a low pressure discharge-flow system. The integrated band strengths for the ν_1 (3400 cm^{-1}), ν_2 (1400 cm^{-1}) and ν_3 (1100 cm^{-1}) bands are 20 ± 6 , 58 ± 16 , and $35 \pm 9\text{ cm}^{-2}\text{ (STP atm)}^{-1}$. We have combined our individual linestrength results with an atmospheric transmission model in order to predict the optimal spectral regions for stratospheric measurements of HO_2 by infrared absorption. Two sets of nearly coincident line pairs in the ν_2 band at 1371.927 and at 1411.180 cm^{-1} , both of which have combined line intensities of $1.5 \times 10^{-20}\text{ cm}^{-2}\text{ molecule}^{-1}\text{ cm}^{-1}$ at 225 K , are relatively free from interference from other atmospheric absorption lines. These line intensities correspond to a fractional absorption in the stratosphere of 1.3×10^{-5} over a 1 km path for an expected HO_2 mixing ratio of 200 ppt at 30 km altitude.

We have also detected H^{18}O_2 radicals with the TDL system and are currently studying the reaction



using isotopic labeling with $^{18}\text{O}_2$ to eliminate interference from the back-reaction of OH product with O_3 to reform HO_2 . The emphasis of this study is on the reaction mechanism and product (^{18}OH or ^{16}OH) in the temperature range 200 to 240 K relevant to the lower stratosphere.

Ozone Isotope Studies

The isomeric distribution of ^{18}O in heavy ozone produced in an electric discharge has been measured using infrared tunable diode laser spectroscopy to distinguish between $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$. Ozone samples with different levels of enhancement in heavy isotopes were analyzed simultaneously by molecular beam mass spectrometry and infrared absorption. Relative to total heavy ozone, the asymmetric $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ molecules are found to make up 4/5 of the enhancement. These results suggest that the mechanism responsible for heavy ozone enhancement in the stratosphere is strongly influenced by molecular symmetry in the $\text{O} + \text{O}_2 + \text{M}$ recombination reaction.

These heavy ozone studies have been done in collaboration with J. Morton and K. Mauersberger at the University of Minnesota.

Thermochemistry of Stratospheric Aerosols Compounds

Heterogeneous reactions on aerosol particles are responsible for the extreme springtime ozone depletions observed in the polar regions and may contribute to mid-latitude chlorine-ozone chemistry. The composition and chemistry of polar stratospheric clouds are crucial to the understanding of this phenomena.

We have initiated laboratory studies in order to determine the thermodynamic properties of the binary solids involving water with HNO_3 , HCl , HBr , and H_2SO_4 . A cryogenic chamber enclosing a multiple-pass infrared absorption cell has been designed, constructed and interfaced with a tunable diode laser spectrometer to measure vapor pressures of these molecules in equilibrium with ice-solid solutions and the relevant crystalline hydrates at stratospheric temperatures.

These studies are being conducted in collaboration with S. Wofsy and L. Fox from Harvard University.

JOURNAL PUBLICATIONS

Mark S. Zahniser, Keith E. McCurdy, and Alan C. Stanton, "Quantitative Spectroscopic Studies of the HO_2 Radical: Band Strength Measurements for the ν_1 and ν_2 Vibrational Bands," J. Phys. Chem. 93, 1065 (1989).

S.M. Anderson, J. Morton, and K. Mauersberger, "Laboratory Measurements of Ozone Isotopomers by Tunable Diode Laser Absorption Spectroscopy," Chem. Phys. Lett. 156, 175 (1989).

PHOTOCHEMISTRY OF THE UPPER ATMOSPHERE

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Objectives

To conduct laboratory studies of stratospheric photochemistry, including absorption cross sections, photolytic quantum yields, reaction mechanisms, and product distributions.

Progress

A study of the chemical and UV spectral properties of the ClO dimer has been made. The dimer was prepared by static photolysis of $\text{Cl}_2\text{-O}_3$ and $\text{Cl}_2\text{-Cl}_2\text{O}$ mixtures in the temperature range 195-218K. The experiments were conducted both in the gas phase and in cryogenic solvents such as liquid CF_4 , CO_2 , and N_2O . Accurate UV cross-sections in the wavelength range 190-400 nm were obtained in the gas phase and in the liquid media. No evidence was found for any dimer structure other than the symmetric form, ClOOC l . It was further shown that the dimer does not react with O_3 within this temperature range, and a rate constant upper limit of 1×10^{-19} cm/molec-sec was established.

Photolysis of $\text{O}_3/\text{H}_2\text{O}/\text{CO}$ mixtures at 184.9 nm was used to measure the steady-state ozone concentrations in these mixtures, which can be shown to depend only on the rate constant ratio

$$k(\text{HO}_2 + \text{O}_3)/k(\text{HO}_2 + \text{HO}_2)^{1/2}$$

The results were used to test the current best values, as recommended by the NASA Data Evaluation Panel, for the directly measured individual values for the two rate constants. The results showed that the recommended rate constants reproduce the observed ozone steady states to about 25%, which is within the stated error limits. The observed ozone concentration was higher than that predicted by the recommended rate constants. In a related series of experiments, tests were made for a pressure dependence of the $\text{OH} + \text{HO}_2$ reaction in the pressure range near one atmosphere, and none was found.

Publications

1. "Yields of $\text{O}_2(\text{a})$ and $\text{O}_2(\text{b})$ in the $\text{H} + \text{O}_2$ Reaction System, and the Quenching of $\text{O}_2(\text{b})$ by Atomic Hydrogen", Internat. J. Chem. Kin. 20, 915 (1988).
2. "UV Spectrum and Chemical Reactivity of the ClO Dimer", W. B. DeMore and E. T. Roux, paper presented at the Second International Conference on Chemical Kinetics, Gaithersburg, MD, July, 1989.

ATMOSPHERIC PHOTOCHEMISTRY
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Objectives

This task is aimed at measuring in the laboratory rate constants and photochemical parameters for reactions which are potentially important in the stratosphere. The experiments involve both homogeneous and heterogeneous systems; the pressure and temperature ranges covered include those characteristic of the polar stratosphere. The systems under study include the photochemistry of Cl_2O_2 ; the vapor pressures of HCl on ice-like substrates related to polar stratospheric clouds; and heterogeneous chemistry of ClONO_2 on these substrates. The experimental techniques employed include laser photolysis, vacuum UV resonance fluorescence, FTIR and UV spectrophotometry, and mass spectrometry.

Summary of Program and Results

The quantum yield for the photodissociation of Cl_2O_2 at 308 nm has been measured to be unity, within experimental error, for the production of Cl-atoms and ClOO radicals. The ClOO species has been found to be less stable than previously thought; it decomposes very fast yielding Cl-atoms and O_2 molecules.

The solubility of HCl in various ices has been investigated. Pure water-ice readily absorbs HCl vapor, forming a hexahydrate, but only at HCl partial pressures above about 10^{-5} torr. At lower partial pressures nitric acid trihydrate and impure ices have a stronger affinity for HCl, and these are the solid substrates that are expected to efficiently promote heterogeneous chemical processes in the stratosphere.

Publications

1. Antarctic Stratospheric Chemistry of Chlorine Nitrate, Hydrogen Chloride, and Ice: Release of Active Chlorine, M. J. Molina, T. L. Tao, L. T. Molina, and F. C.-Y. Wang, Science, 238, 1253, 1987.
2. Interactions between HCl, NO_x and H_2O -Ice in the Antarctic Stratosphere: Implications for Ozone, J. Geophys. Res. 93, 2442, 1988.
3. The Antarctic Ozone Hole, M. J. Molina, Oceanus, 31, 47, 1988.
4. Primary quantum yields of Cl_2O_2 photodissociation, M. J. Molina, A. Colussi, R. Schindler, L. T. Molina and T. L. Tso, in preparation, to be submitted to J. Phys. Chem.

A. Title of Research Task: STUDY OF THE ATMOSPHERIC CHEMISTRY OF NO_y SPECIES

B. Investigators and Institutions: Jack G. Calvert, James A. Davidson, Christopher A. Cantrell, Richard E. Shetter, Anthony H. McDaniel, and Geoffrey S. Tyndall, Atmospheric Chemistry Division, National Center for Atmospheric Research, Box 3000, Boulder, CO, 80307.

C. Abstract of Research Objectives: Kinetic and spectroscopic studies will be made of several NO_y species (NO₃, N₂O₅, NO₂, CH₃COO₂NO₂) which are important in the atmosphere and for which significant uncertainties in the reaction pathways remain. Rate constants for the following NO₃ reactions will be studied in flow and static systems using several spectroscopic and chemical techniques at a variety of temperatures and pressures characteristic of the troposphere and stratosphere: NO₃ + NO → 2NO₂ (1); NO₂ + NO₃ → NO + NO₂ + O₂ (2); NO₂ + NO₃ (+M) → N₂O₅ (+M) (3), and N₂O₅ (+M) → NO₃ + NO₂ (+M) (4). The nature of the primary processes and their quantum yields for NO₃ photodissociation as a function of wavelength and temperature will be determined: NO₃ + hν → NO₂ + O (5); NO₃ + hν → O₂ + NO (6). Several measurements which bear on the atmospheric chemistry of NO₂ will be made: a) the temperature dependence of the quantum yields and cross sections of NO₂ in the 397.9 to 420 nm range using low intensity laser beam excitation; b) measurements of the rate constant for the reaction: HO₂ + NO₂ → HONO + O₂ (7). New data related to the atmospheric properties of peroxyacetyl nitrate (PAN) will be determined: a) temperature dependence of the cross sections for PAN; b) rate constants for the suggested molecular rearrangements of PAN: CH₃COO₂NO₂ → CH₃ONO₂ + CO₂ (8), and CH₃COO₂NO₂ → CH₃CO + NO₃ (9). Finally studies will be undertaken to access the kinetics and products of the reaction of the NH₂ radical with O₂.

D. Summary of Progress and Results:

Laser systems have been installed in a newly completed laser laboratory designed for these studies; rare gas, pulsed excimer and CW argon ion lasers are used to drive dye laser systems employed in these kinetic and spectroscopic studies.

Laboratory experiments were performed to measure the ratio of rate constants k_1/k_2 for the reactions: NO₃ + NO → 2NO₂ (1) and NO₂ + NO₃ → NO + NO₂ + O₂ (2), respectively. This was accomplished through direct measurements of the nitric oxide and nitrogen dioxide concentrations in an N₂O₅/NO₂/N₂ mixture. The NO was measured with NO/O₃ chemiluminescence, and the NO₂ was determined through long-path visible absorption spectroscopy. When the measured ratio is combined with recent measurements of k_1 , then a value for k_2 is calculated which is in reasonable agreement with other recent measurements from this laboratory.

A fast flow apparatus has been constructed to measure NO₃ rate coefficients by laser induced fluorescence. The NO₃ fluorescence is excited at 623 nm with light from the argon ion-pumped ring dye laser. The reaction of NO₃ with NO has been studied by following the kinetics of NO₃ in excess NO. At temperatures below 298 K the results are in good agreement with Hammer et al. (*J. Chem. Phys.*, 90, 2491-2496, 1986). At 298 K, $k \approx 2.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; E/R \approx 1 -200 K. Experiments are in progress to establish the degree of curvature of the Arrhenius

plot for temperatures above 298 K. Experiments will be carried out using excess NO_3 , detecting NO by chemiluminescence to check if any curvature of the Arrhenius plot observed in previous work results from secondary reactions of NO_3 .

A temperature controlled (-80 to 200°C) reaction cell has been designed for use in planned kinetic studies of N_2O_5 decay at high pressures (up to 400 psi). It is constructed of stainless steel with a 4 meter path length which will allow detection of the reactant gases by means of a visible, uv, and IR Fourier transform spectrometer or diode array spectrometer systems.

E. Journal Publications on NASA Sponsored Research During 1988 and 1989

1. The equilibrium constant for $\text{N}_2\text{O}_5 = \text{NO}_3 + \text{NO}_2$: absolute determination by direct measurement from 243 to 397 K, C. A. Cantrell, J. A. Davidson, A. H. McDaniel, J. G. Calvert, and R. E. Shetter, *J. Chem. Phys.*, **88**, 4997-5006, 1988.
2. The enthalpy of formation of dinitrogen pentoxide and nitrate free radical, A. H. McDaniel, J. A. Davidson, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.*, **92**, 4172-4175, 1988.
3. Visible-ultraviolet absorption cross sections for NO_2 as a function of temperature, J. A. Davidson, C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich, and J. G. Calvert, *J. Geophys. Res.*, **93**, 7105-7112, 1988.
4. Temperature dependence of the atmospheric photolysis rate coefficient for NO_2 , R. E. Shetter, J. A. Davidson, C. A. Cantrell, N. J. Bursynski, Jr., and J. G. Calvert, *J. Geophys. Res.*, **93**, 7113-7118 (1988).
5. Infrared absorption cross sections for N_2O_5 , C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, *Chem. Phys. Lett.*, **148**, 358-363, 1988.

B. SPECTROSCOPY

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NASA Upper Atmosphere Research Program: 1988-89 Research SummaryA. Title: Inelastic Collision Processes in Ozone and their Relation to Atmospheric Pressure Broadening

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C Abstract of Research Objectives

This research task employs infrared double-resonance to determine rotational energy transfer rates and pathways, in both the ground and vibrationally excited states of ozone. The resulting data base will then be employed to test inelastic scattering theories and to assess intermolecular potential models, both of which are necessary for the systematization and prediction of infrared pressure-broadening coefficients, which are in turn required by atmospheric ozone monitoring techniques based on infrared remote sensing. In addition, observation of excited-state absorption transitions will permit us to improve the determination of the $2\nu_3$, $\nu_1+\nu_3$, and $2\nu_1$ rotational constants and to derive band strengths for hot-band transitions involving these levels.

D. Summary of Progress and Results

Work on this program, with NASA support, began in March of 1989. Our initial efforts have been directed toward setting up the experimental apparatus necessary for carrying out the double-resonance measurements, acquiring a spectroscopic data base for ozone, and devising a strategy for theoretical interpretation of the anticipated results. To date, the following tasks have been accomplished:

1) An ozone-compatible vacuum system and double-resonance cell have been assembled, capable of preparing ozone samples of up to 90% purity or in mixtures with buffer gases, and holding these samples at a controlled temperature for a period of time sufficient to carry out experiments.

2) A set of lead-salt diode lasers has been ordered and tested for operation in the $1000 - 1050 \text{ cm}^{-1}$ region, corresponding to the $\nu_3 \leftarrow 0$, $2\nu_3 \leftarrow \nu_3$, and $\nu_1+\nu_3 \leftarrow \nu_1$ absorption regions of ozone.

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3) We have received the ozone line listing from NASA Ames Research Center via Bitnet, along with selected portions of the FT-IR absorption spectrum. Since some of the hot-band line-center positions have been revised in the most recent (1989) update, we will need to incorporate these revisions in our database.

4) Transient three-level double resonance signals have been obtained for the ($2\nu_3-\nu_3$, $184_{14} - 174_{13}$) transition in ozone when the (ν_3-0 , $174_{13} - 164_{12}$) transition is pumped with the CO₂ laser at 1053.92 cm⁻¹. Both rotational and vibrational relaxation decays may be observed at different time scales, as shown in Fig. 1. A search is now in progress for additional signals in the ν_3-0 , $2\nu_3-\nu_3$, and $\nu_1+\nu_3-\nu_1$ bands, following which the relaxation rates will be measured as a function of ozone and buffer-gas pressures and temperature.

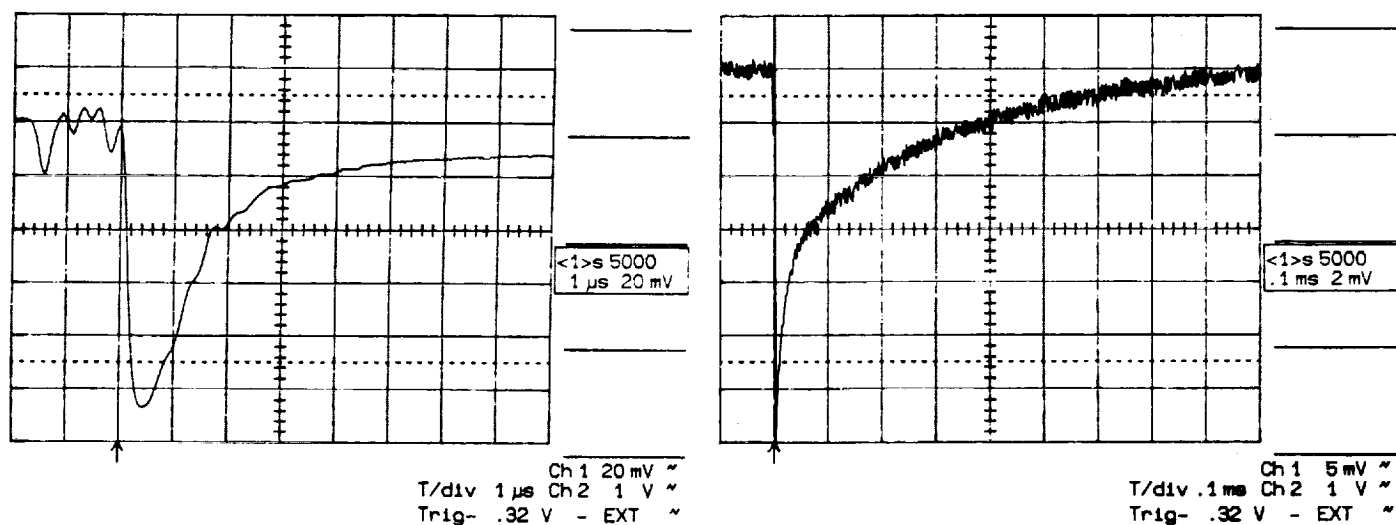


Figure 1. 3-level double-resonance (excited-state absorption) on the ($2\nu_3-\nu_3$, $184_{14}-174_{13}$) transition in ozone (0.25 Torr). The fast decay in the left trace is due to rotational relaxation, while the slower decay, with smaller amplitude, shown in the right-hand trace is due to vibrational relaxation of the rotationally equilibrated $\nu_3=1$ level.

5) Theoretical analysis will focus on validation of the Quantum Fourier Transform (QFT-ID) theory developed by Dr. R. Gamache of the University of Lowell. In initial discussions with Dr. Gamache, we have developed a strategy for extracting final-state-specific transition probabilities from his calculations, which will then be compared with the state-to-state measurements resulting from our experiments.

E. PUBLICATIONS

J. Steinfeld, B. Foy, J. Hetzler, C. Flannery, J. Klaassen, Y. Mizugai, and S. Coy, "Determination of Molecular Spectroscopic Parameters and Energy Transfer Rates by Double Resonance Spectroscopy", Proceedings, Workshop/Conference on Laboratory Research for Planetary Atmospheres (Bowie, Md, Oct. 1989)

Title: Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere

Investigators and Institutions: C. Chackerian, Jr.(P.I.), L. P. Giver, D. Goorvitch , M. Spencer, F.P.J. Valero, NASA Ames Research Center.

Abstract of Research Objectives:

We obtain quantitative laboratory spectroscopic measurements of molecular constituents which are of importance in understanding the "health" of the Earth's atmosphere, and in particular emphasize those species which are important for understanding stratospheric kinetics or are used for long term monitoring of the stratosphere. Our measurements provide: (1) line and band intensity values which are needed (a) to establish limits of detectability for as yet unobserved species and (b) to quantify the abundance of those species which are observed, (2) line-positions, -half widths and pressure induced shifts are all needed for remote sensing techniques, and (3) data on the above basic molecular parameters at temperatures and pressures appropriate for the real atmosphere.

Summary of Progress and Results:

The Herman-Wallis effect was used to obtain absolute line intensities for a number of free radical diatomic molecules: at the end of 1987 journal articles were published on absolute ro-vibrational intensities for the $\text{C}\ell\text{O}$ and CS radical species and subsequently absolute ro-vibrational line intensities have been determined for the NH and SH molecules. We are currently working on spectra of OH which in one scan extend from the pure rotational region, starting about 350 cm^{-1} , thru the $\Delta V=1$ ro-vibration bands which are centered around 3500 cm^{-1} . We hope to obtain absolute line intensities with this data using a generalized Herman-Wallis approach. We have made low temperature N_2 - broadening measurements on O_3 lines in the 1040 cm^{-1} spectral region using a 6 cm teflon coated low temperature cell. The construction of a 30 cm low temperature absorption cell is nearly completed. It is made of copper with an acid resistant stainless steel liner and should be coolable to 150 K. Diode laser spectra have been obtained of highly purified samples of $\text{C}\ell\text{ONO}_2$ in the 780.2 cm^{-1} spectral region. Some structure in these spectra offer hope that the intensities can be understood at the line by line level. Laboratory spectra obtained at Kitt Peak (with L. Brown, J.P.L.) on the 1450 cm^{-1} band of $\text{CH}_3\text{C}\ell$ will be used to estimate atmospheric abundance from ATMOS spectra.

Journal Publications(1988-1989):

1. S.D. Gasster, C.H. Townes, D. Goorvitch and F.P.J. Valero, "Foreign-gas collision broadening of the far-infrared spectrum of water vapor", J. Opt. Soc. B. 5, 593 (1988).
2. C. Chackerian, Jr., "The Determination of Absolute Ro-vibrational Intensities for Radical Diatomic Molecules", J. Quant. Spectrosc. Rad. Transfer 40, 195 (1988).
3. C. Chackerian, Jr., G. Guelachvili, A. Lopez-Piniero and R. Tipping, "Ro-vibrational Intensities for the $\Delta V = -1$ bands of the $\text{X } ^3\Sigma$ NH radical: experiment and theory", J. Chem. Phys. 90, 641 (1989).
4. C. Chackerian, Jr., D. Goorvitch and L. Giver, " N_2 -broadening in the HCL Vibrational Fundamental: Temperature Dependence between 160 and 296 K", J. Quant. Spectrosc. Rad. Transfer (submitted).
5. C. Chackerian, Jr., N. Lacome, A. Levy, Collisional Line Mixing, in "Spectroscopy of the Earth's Atmosphere and Interstellar Molecules" (K. N. Rao and A. Weber, eds) Academic Press (in press).

A. "Laboratory Spectroscopy in Support of Atmospheric Measurements"

RTOP # 147-23-02

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J. Butler, STX Corp.

C. Abstract of Research Objectives

Optical Measurements of Trace Species in the atmosphere require precise, accurate spectroscopic data for the molecules under study. This laboratory exists to provide high quality spectroscopic data for the interpretation of data from existing satellite balloon, ground and aircraft instruments, as well as to provide sufficient data to assess the feasibility of new instruments.

D. Summary

Work in FY 89 has centered the time resolved, rotationally resolved fluorescence spectroscopy in OH radicals. The importance is derived from fluorescence lidar measurements of OH in the stratosphere, and a need to understand the collisional redistribution of energy in the excited state in order to interpret the field measurements. The laboratory has studied effects of collisions with O₂ and N₂ on excited state OH molecules for both the v'=0 and v'=1 levels. In addition to electronic quenching rates, total

deactivation out of populated rotational levels has also been measured. This work is currently being expanded to include measurements at stratospheric temperatures.

E. Publications

1. "Collisional Deactivation and Rotational Transfer Rates in the $A^2\Sigma^+(v'=1)$ State of OH," J. Burris, J. Butler, T. J. McGee and W. S. Heaps, Chem. Phys., 124, 251, 1988.
2. "Quenching and Rotational Transfer Rates in the $A^2\Sigma^+(v'=0)$ Manifold of OH," J. Burris, J. Butler, T. J. McGee, and W. S. Heaps, to be submitted to Chemical Physics.

A. DETERMINATION OF SPECTROSCOPIC PROPERTIES OF ATMOSPHERIC MOLECULES
FROM HIGH RESOLUTION VACUUM ULTRAVIOLET CROSS SECTION AND WAVELENGTH
MEASUREMENTS

B. W.H. Parkinson, Principal Investigator
K. Yoshino and D.E. Freeman, Co-Investigators

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C. ABSTRACT OF RESEARCH OBJECTIVES

The research objectives are (a) the comprehensive high resolution spectroscopic investigation of the absorption spectra, cross sections and the predissociation line widths of the Schumann-Runge bands of oxygen in the wavelength region 175-205 nm and the determination of improved absorption continuum cross sections of oxygen in the 205-240 nm region of the Herzberg continuum; and (b) the measurement of the absolute absorption cross section of ozone, and its temperature dependence, in the region 180-340 nm. These absorption bands play a critical role in the photochemistry of the upper atmosphere.

D. SUMMARY OF PROGRESS AND RESULTS

Cross sections of $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ at 79 K have been obtained from photoabsorption measurements in the wavelength region 177-198 nm with a 6.65 m photoelectric scanning spectrometer. The measured absorption cross sections of the $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ Schumann-Runge bands (11,0) through (3,0) are independent of the instrumental width. The measured cross sections are presented graphically and are available at wavenumber intervals of $\sim 0.1 \text{ cm}^{-1}$ on magnetic tape from the National Space Science Data Center, NASA/Goddard Space Flight Center. Band oscillator strengths have been determined by numerical integration of the measured absolute cross sections and are in agreement with our theoretically calculated values.

High resolution absorption spectra of $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ have been photographed, at 300 K and 78 K, throughout the region 175-205 nm. Precise wavelength measurements and rotational analyses of the Schumann-Runge bands have been completed. Spectroscopic constants of the $B^3\Sigma_u^-$ states have been determined. The concept of mass-reduced vibrational quantum numbers has been used to combine isotopic molecular constants from $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$. Values of molecular constants have been obtained by interpolation for bands with unresolved triplet structure. Excellent agreement between calculated and experimental level shifts has been obtained for all three isotopic molecules.

The laboratory values of the Herzberg continuum absorption cross section of oxygen at room temperature from Cheung *et al.* [Planet. Space

Sci. (1986) 34, 1007] and Jenouvrier et al. [Planet. Space Sci. (1986) 34, 253 and J. Quant. Spectrosc. Radiat. Transfer (1986) 36, 349] have been compared and reanalyzed. These values have been combined to obtain improved values of the Herzberg continuum cross section throughout the wavelength region 205-240 nm.

We have completed measurements of the absorption cross sections of the Schumann-Runge bands in the window regions between the rotational lines in the wavelength region 180-195 nm. The measurements have been done with many different pressures of oxygen, 50-760 Torr, so that the pressure dependent absorption can be separated from the main cross sections.

Measurements of the absolute absorption cross section of ozone at the temperatures 195 K, 228 K, and 295 K have been made at discrete wavelengths in the region 238-335 nm. Our absolute cross sections have been used to put our recent relative cross section measurements on a firm absolute basis.

E. JOURNAL PUBLICATIONS

Absolute Absorption Cross Section Measurements of Ozone in the Wavelength Region 238-335 nm and the Temperature Dependence, K. Yoshino, D.E. Freeman, J.R. Esmond, and W.H. Parkinson, Planet. Space Sci. 36, 395-398 (1988).

Wavelength Measurements and Analysis of the Schumann-Runge Bands of $^{18}\text{O}_2$ in the Region 175-205 nm, A.S.-C. Cheung, K. Yoshino, D.E. Freeman and W.H. Parkinson, J. Mol. Spectrosc. 131, 96-112 (1988).

High Resolution Absorption Cross Sections and Band Oscillator Strengths of the Schumann-Runge Absorption Bands of Isotopic Oxygen, $^{18}\text{O}_2$, at 79K, K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 36, 1201-1210 (1988).

Improved Absorption Cross Sections of Oxygen in the Wavelength Region 205-240 nm of the Herzberg Continuum, K. Yoshino, A.S.-C. Cheung, J.R. Esmond, W.H. Parkinson, D.E. Freeman, S.L. Guberman, A. Jenouvrier, B. Coquart, and M.F. Merienne, Planet. Space Sci. 36, 1469-1475 (1988).

The Schumann-Runge Bands of $^{16}\text{O}^{18}\text{O}$ in the Wavelength Region 175-205 nm and Spectroscopic Constants of Isotopic Oxygen Molecules, A.S.-C. Cheung, K. Yoshino, D.E. Freeman R.S. Friedman, A. Dalgarno and W.H. Parkinson, J. Mol. Spectrosc. 134, 362-389 (1989).

High Resolution Absorption Cross Sections and Band Oscillator Strengths of the Schumann-Runge Absorption Bands of Isotopic Oxygen, $^{16}\text{O}^{18}\text{O}$, at 79K, K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 37, 419-426 (1989).

A. INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF STRATOSPHERIC MEASUREMENTS INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOS

B. Principal investigator: Robert A. Toth
Co-Investigator: Linda R. Brown
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C. ABSTRACT OF RESEARCH OBJECTIVES

The objective of this program is the acquisition and analysis of molecular spectral parameters for the 2 to 16 μm region in order that data obtained from stratospheric measurements programs can be properly interpreted. Field instruments such as the Atmos and Mark IV interferometers have spectral resolutions of 0.01 cm^{-1} and 0.005 cm^{-1} , respectively, which require that laboratory measurements, which support these efforts, be obtained at comparable or better spectral resolutions.

For this program, conventional spectroscopic techniques are used to analyze infrared spectra obtained in the laboratory. Spectra are recorded at 0.0028, 0.005 and 0.01 cm^{-1} resolutions using an interferometer located in the McMath facility at the Kitt Peak National Observatory. The gases studied include the normal trace species such as H_2O , CO_2 , CH_4 , and N_2O and less abundant trace gases such as H_2CO , NO_2 , COF_2 , and CH_3Cl . The molecules of the first category produce absorptions over wide expanses of the stratospheric spectrum which, in many cases, overlap or blend with spectral features of the less abundant species. Therefore, in order to obtain an accurate estimate of the stratospheric concentration of the less abundant gases using infrared techniques requires not only an accurate estimate of the line parameters of these species but also a detailed knowledge of the line parameters of the normal trace gases.

D. SUMMARY OF PROGRESS AND RESULTS

Our efforts have been focused on compiling accurate spectral parameters derived from laboratory measurements for use in the reduction of stratospheric data. A large portion of this compilation has already been used in the various analysis of ATMOS spectra obtained from Spacelab 3. Listings of spectral parameters derived from our laboratory measurements which are presently available to ATMOS investigators include the following: N_2O (500-4100 cm^{-1}), CH_4 (1100-4700 cm^{-1}), NO_2 (1520-1660 cm^{-1}), HDO (1000-4400 cm^{-1}), CO_2 (1200-1400 cm^{-1}), and H_2^{16}O , H_2^{17}O , and H_2^{18}O (900-4400 cm^{-1}).

During 1988 and 1989, additional spectra of water vapor (four isotopic species), methane (two isotopic species), methyl chloride and calibration standards were obtained with a Fourier transform spectrometer located at the Kitt Peak National Observatory (KPNO). Also on computer files, we have a large number of spectra of other molecules (N_2O , NO_2 , CO_2 , CO , COF_2 , HNO_3 , HCOOH , H_2CO , CF_4 , OCS ,) recorded at KPNO on earlier dates. Molecular parameters for a number of molecules were obtained from which several papers were published or are in preparation.

Improved line lists of N_2O , NO_2 , H_2O , CH_4 and CO_2 were created from the analysis of laboratory measurements. In addition, assistance was given to ongoing studies of O_3 , COF_2 , and H_2O_2 that were previously initiated by other investigators. Also, in response to the needs of ATMOS, analyses of some heavier molecules (HNO_3 , COF_2 , CF_4 and several chlorofluorocarbons) were performed in spectral regions of stratospheric interest in which empirical fits of the laboratory data were obtained. The latter is an ongoing task and will continue.

E. PUBLICATIONS

1. J. P. Champion, J. C. Hilico and L. R. Brown, "The vibrational ground state of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. **133**, 244-255 (1989).
2. J. P. Champion, J. C. Hilico, C. Wenger and L. R. Brown "Analysis of the ν_2/ν_4 Dyad of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. **133**, 256-272 (1989).
3. L. R. Brown, M. Loete and J. C. Hilico, "Line strengths of the ν_2 and ν_4 bands of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$," J. Mol. Spectrosc. **133**, 273-311 (1989).
4. R. A. Toth, E. A. Cohen and R. L. Poynter, "Line frequencies and absolute strengths in the (010)-(000) band of H_2^{16}O ," J. Am. Opt. Soc. (in press).
5. L. R. Brown and E. A. Cohen, "Assignment of the ν_1 and $2\nu_2$ bands of COF_2 at $5.2\text{ }\mu\text{m}$," 44th Symposium on Molecular Spectroscopy, Abstract RE7, Ohio State University (1989).
6. R. A. Toth, "New measurements and analysis of H_2^{16}O , H_2^{17}O and H_2^{18}O in the $6.2\text{ }\mu\text{m}$ region," 44th Symposium on Molecular Spectroscopy, Abstract TE12, Ohio State University (1989).
7. R. A. Toth, "Line strengths ($1100\text{-}2370\text{ cm}^{-1}$), self broadened line widths and frequency shifts ($1800\text{-}2630\text{ cm}^{-1}$) of N_2O (submitted to J. Am. Opt. Soc.).

A. LASER LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOSPHERIC MEASUREMENTS

B. Principal Investigator: Dr. Randy D. May

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C. Abstract of Research Objectives

The laser laboratory spectroscopy program involves the acquisition and analysis of high-resolution molecular spectral data which are required for the interpretation of atmospheric measurements by infrared instruments such as the BLISS and ALIAS diode laser spectrometers and FTIR instruments. These data are also required to define the optimum spectral regions to be used for detection of a particular molecular species, to establish the feasibility of new spectroscopic techniques for in-situ and remote sensing of Earth and planetary atmospheres, and to test current theories of molecular lineshape variations with pressure, temperature and gas composition.

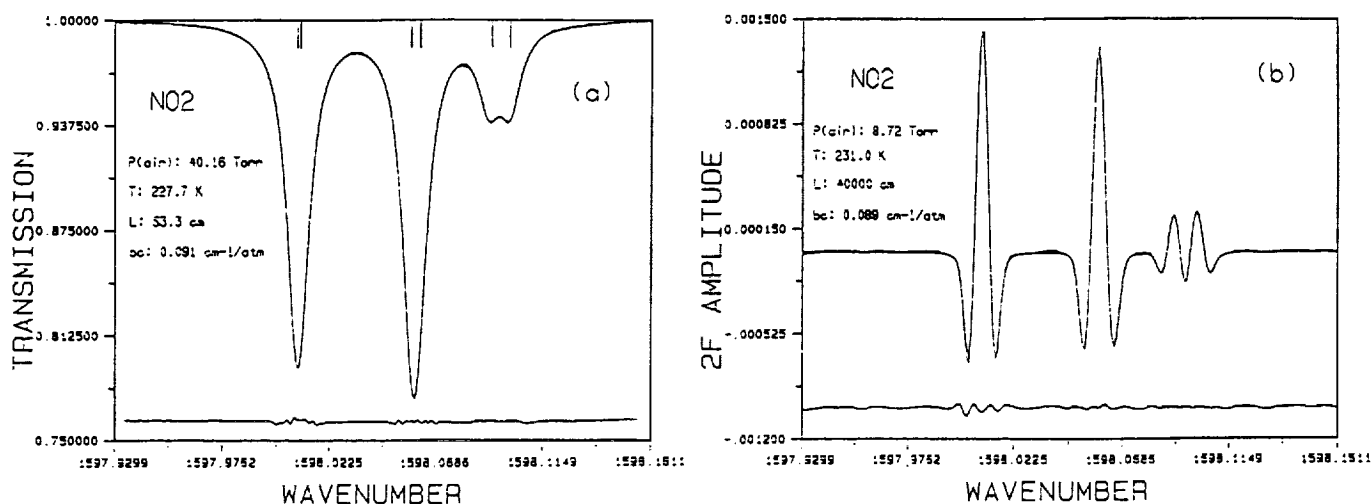
D. Summary of Progress and Results

Measurements have been made, for the first time, of the spectral response of a pressure modulated radiometer using a high-resolution tunable diode laser spectrometer. Recorded lineshapes of selected lines of N_2O , H_2O and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ were interpreted using one- and two-pressure approximations for the mean and modulated transmission signals, respectively.

A coolable (to 200 K) 1/2 m absorption cell was constructed and used to measure collisional line broadening coefficients for several molecular species important in stratospheric photochemistry. Air-broadening coefficients were measured as a function of temperature for NO_2 near 1600 cm^{-1} , HNO_3 in the $1290 - 1340\text{ cm}^{-1}$ region, and O_3 near 1065 cm^{-1} . For HNO_3 , line positions and intensities were also measured for approximately 1000 lines in the 7.5 micron bands to provide data needed for completion of the rotational analysis of the overlapping ν_3 and ν_4 bands. These measurements were utilized in the analysis of data from two recent flights of the BLISS balloon-borne diode laser spectrometer.

A complete set of data acquisition and analysis software has been developed for recording and processing infrared spectral data on a laboratory minicomputer. Sophisticated interactive spectral fitting routines allow

accurate processing of both direct transmission and harmonic diode laser spectra. Currently, implementation of RF modulation techniques, which enable quantum noise-limited detection sensitivities to be realized, is underway with applications in both laboratory and field measurement programs utilizing tunable diode lasers.



Air-broadened transmission (a) and second harmonic (b) NO₂ spectra

E. Journal Publications

1. R.D. May, D.J. McCleese, D.M. Rider, J.T. Schofield, and C.R. Webster, "Tunable Diode Laser Spectral Diagnostic Studies of a Pressure Modulated Radiometer", *Appl. Optics* **27**, 3591 (1988).
2. R.D. May, "Computer Processing of Tunable Diode Laser Spectra", *J. Appl. Spectrosc.*, **43**, 834 (1989).
3. R.D. May and C.R. Webster, "Measurements of Line Positions, Intensities, and Collisional Air-Broadening Coefficients in the HNO₃ 7.5 micron Band using a Computer-Controlled Diode Laser Spectrometer", *J. Molec. Spectrosc.* (submitted, 1989).
4. R.D. May and C.R. Webster, "Temperature Dependence of NO₂ Air-Broadening Coefficients near 1600 cm⁻¹", (in preparation).

A. Title of Research Task

Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

B. Investigators

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C. Abstract of Research Objectives

A program of millimeter and submillimeter spectroscopy research is conducted in support of upper atmospheric research. This includes laboratory studies, critical analysis of data from all available sources, generation of line list catalogs, and distribution of results to the field measurement community. The program involves the acquisition and analysis of molecular spectral parameters which are required for the interpretation of data from stratospheric measurements. The laboratory spectral measurements specifically supports the JPL millimeter radiometer instruments. In order to take full advantage of spectroscopic techniques for quantitative atmospheric measurements, emphasis is placed on performing accurate line frequency, line width, and transition moment measurements. A large portion of the spectral data is also of value to other groups which use spectroscopic techniques for atmospheric measurements. This will be cataloged in a continuously upgraded millimeter data base and made available to interested users. Recently this program has provided valuable molecular structural information which has direct bearing on proposed mechanisms for polar ozone destruction. Work in this area will continue.

D. Summary of Progress and Results

Contributions to the JPL "Microwave, Millimeter, and Submillimeter Spectral Line Catalog" continued with entries being added for $\text{CH}_3^{35}\text{Cl}$, $\text{CH}_3^{37}\text{Cl}$, COF_2 , $^{16}\text{O}^{17}\text{O}$ and H_2^{17}O . Significant improvements in the predicted rotational line strengths of O_3 and H_2O have been achieved by careful consideration of vibration rotation interactions. The rotational wave functions for H_2O which were generated during the updating of the catalog have been used to refine the intensity calculations of the ν_2 band in the $1000\text{--}2600\text{ cm}^{-1}$ region. COF_2 ground state parameters have been improved and used in the analysis of the ν_1 and $2\nu_2$ infrared bands.

A new analysis of the microwave, far infrared, and infrared spectra of transitions involving the (010) and (020) levels of O_3 markedly improved the agreement with observations of both positions and strengths in the 700 cm^{-1} region.

The analysis of the linewidth measurements of the N_2 and O_2 broadened O_3 line near 206 GHz was refined so as to be useful for MLS pointing determinations.

The N_2O_5 millimeter wave spectrum is being re-investigated. Some weak lines have been observed and measured for the first time, but the spectrum remains unassigned.

A gas flow reactor for the synthesis of ClO dimer has been used with the submillimeter wave spectrometer. The dimer's rotational spectrum has been unambiguously observed in the millimeter and submillimeter regions. The rotational transitions of the ground and first excited torsional states of the peroxide structure have been assigned for the 35-16-16-35 and 35-16-16-37 isotopic species. All structural parameters have been determined. It has been demonstrated that ClOOCl is the principal product of the ClO gas phase self reaction at low temperature.

E. Journal Publications

1. H. M. Pickett, E. A. Cohen, L. R. Brown, C. P. Rinsland, M. A. H. Smith, V. Malathy Devi, A. Goldman, A. Barbe, B. Carli, and M. Carlotti, "The Vibrational and Rotational Spectra of Ozone for the (0,1,0) and (0,2,0) States," *J. Mol. Spectrosc.*, **128**, 151 (1988)
2. M. Birk, R. R. Friedl, E. A. Cohen, H. M. Pickett, and S. P. Sander, "The Rotational Spectrum and Structure of Chlorine Peroxide," *J. Chem. Phys.*, in press.
3. Y. Koga, H. Takeo, S. Kondo, M. Sugie, C. Matsumura, G. A. McRae and E. A. Cohen, "The Rotational Spectra, Molecular Structure, Dipole Moment and Hyperfine Constants of HOBr and DOBr," *J. Mol. Spectrosc.*, in press.
4. G. A. McRae and E. A. Cohen, "The ν_2 Band of HOBr," *J. Mol. Spectrosc.*, in press.

Investigators and Institutions

P.I.: Dr. Mary Ann H. Smith, NASA Langley Research Center
 Co-I's: Dr. V. Malathy Devi, College of William and Mary
 Williamsburg, VA
 Dr. Curtis P. Rinsland, NASA Langley Research Center
 Dr. D. Chris Benner, College of William and Mary
 Mr. Gale A. Harvey, NASA Langley Research Center

Abstract of Research Objectives

Detailed knowledge of the molecular spectra of ozone and other infrared-active atmospheric species is needed for accurate calculation of atmospheric heating and cooling rates in climate models. Remote sensing experiments on the Nimbus-7 satellite and the Spacelab-3 shuttle mission have shown that space-based measurements of infrared absorption or emission can be used to accurately determine the concentrations and distributions of stratospheric species on a global scale. The objective of this research task is to improve knowledge of the spectroscopic line parameters (positions, intensities, assignments, halfwidths, and pressure-induced shifts) of key atmospheric constituents through laboratory measurements.

Summary of Progress and Results

We have recorded a new series of laboratory spectra of ozone at wavelengths between 2 and 5 μm . These measurements utilized the McMath high-resolution Fourier Transform Spectrometer (FTS) at the National Solar Observatory on Kitt Peak, Arizona. Over 18 vibration-rotation bands of $^{16}\text{O}_3$ have already been identified in these spectra. Data analysis is performed primarily at Langley Research Center, and the theoretical interpretation of the results is being done in collaboration with investigators at several other institutions in the United States and France.

Results of this work to date have greatly improved line positions and relative intensities for eight fundamental vibration-rotation bands of the most abundant isotopic form of the ozone molecule ($^{16}\text{O}_3$) in the 3.3 to 3.6 μm region (previously, line positions in most of these bands were known only within $\pm 5 \text{ cm}^{-1}$). The new dataset overlaps our earlier FTS ozone spectra covering the 5-10 μm and 10-15 μm regions; this allows the scaling of line intensities in all ozone bands from 2 to 15 μm to a consistent standard. Analyses of the spectra of ozone in the 3.3 to 3.6 μm region have also resulted in new spectroscopic constants for upper vibration-rotation levels involved in "hot bands" occurring in the 10 μm and 4.8 μm regions. Over 16 "hot bands" have been analyzed in the 10 μm region alone; parameters for many of these bands have previously been unavailable. These laboratory results are now being applied in analyses of atmospheric data. Detailed studies of the broadening of O_3 absorption lines by O_3 , air, and by N_2 using spectra from the McMath FTS and the NASA Langley tunable diode laser (TDL) system are also continuing.

We have also extended our work on the measurement of nitrogen-broadened and air-broadened halfwidths for methane and two of its isotopic variants to the 3 μm region. These studies are based on FTS spectra recorded at Kitt Peak and have resulted in the accurate determination of broadening coefficients and pressure-induced shifts for a large number of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ lines. Our studies have revealed that the halfwidths and shifts of methane lines are not the same for all isotopic species. Comparison of the results in the 3 μm region with those previously obtained in the 7.5 μm region shows small differences in broadening coefficients and large differences in line shifts.

Recently we recorded FTS spectra in the 7.5 μm region of CH_4 broadened by air and by N_2 at temperatures down to -62°C using a coolable absorption cell designed and built at NASA Langley Research Center. Analysis of these spectra to obtain the temperature dependence of air- and N_2 -broadened halfwidths and shifts of CH_4 lines is in progress. All of our research results to date have been reported in the scientific literature and are being made available to public spectroscopic databases.

Journal Publications

Rinsland, C. P.; Smith, M. A. H.; Flaud, J.-M.; Camy-Peyret, C.; and Malathy Devi, V.: Line positions and intensities of the $2\nu_3$, $\nu_1+\nu_3$, and $2\nu_1$ bands of $^{16}\text{O}_3$. J. Mol. Spectrosc., **130**, 204-212 (1988).

Flaud, J.-M.; Camy-Peyret, C.; Rinsland, C. P.; Smith, M. A. H.; and Malathy Devi, V.: Line parameters for $^{16}\text{O}_3$ bands in the 7 μm region. J. Mol. Spectrosc., **134**, 106-112 (1989).

Flaud, J.-M.; Camy-Peyret, C.; N'Gom, A.; Malathy Devi, V.; Rinsland, C. P.; and Smith, M. A. H.: The ν_2 bands of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$: Line positions and intensities. J. Mol. Spectrosc., **133**, 217-223 (1989).

Rinsland, C. P.; Malathy Devi, V.; Smith, M. A. H.; and Benner, D. C.: Measurements of argon-broadened Lorentz width and pressure-induced line shift coefficients in the ν_4 band of $^{12}\text{CH}_4$. Appl. Opt., **28**, 2111-2118 (1989).

Smith, M. A. H.; Rinsland, C. P.; Malathy Devi, V.; Flaud, J.-M.; Camy-Peyret, C.; and Barbe, A.: The 3.6- μm region of ozone: Line positions and intensities. Manuscript submitted to J. Mol. Spectrosc. (1989).

Malathy Devi, V.; Benner, D. C.; Smith, M. A. H.; and Rinsland, C. P.: Measurements of air-, N_2 -, and O_2 -broadened halfwidths and pressure-induced line shifts in the ν_3 band of $^{13}\text{CH}_4$. Manuscript submitted to Appl. Opt. (1989).

A. Title of Research

Infrared Laboratory Measurements on Stratospheric Constituents

B. Investigators and Institutions

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Dr. Walter J. Lafferty (Co-Investigator)
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C. Abstract of Research Objectives

In support of the upper atmospheric measurement program involving infrared measurements from spacecraft, aircraft, and balloon flights as well as ground-based measurements, this project uses high resolution spectra to provide reliable parameters needed to measure the distribution of molecular species of particular interest for understanding the dynamics of atmospheric chemistry. The particular interest of this work is on species involved in the halogen (ClO_x) and nitrogen oxide (NO_x and HNO_x) chemistry cycles. By using techniques, software, and instrumentation developed in this laboratory in recent years, this project measures spectroscopic quantities needed to model atmospheric spectra in order to monitor the distribution of molecular species involved in the chemistry of the upper atmosphere. These data are made available to other workers in the form of molecular parameters as well as in the form of tabulated transition data calculated from the molecular parameters.

D. Summary of Progress and Results

The four low frequency fundamental bands of nitric acid (HNO_3) have been measured and analyzed for the first time. In this work both infrared and microwave measurements were combined to obtain values for the ro-vibrational constants that are needed to calculate the energy levels and transitions responsible for the infrared spectrum.

The moderately strong band at 1205 cm^{-1} was also measured and analyzed. It was shown to be due to the combination band $\nu_8 + \nu_9$.

These bands have been characterized for both line position and relative intensity. The band type has also been characterized. In one case an intensity anomaly was found and measured so that an effective correction term could be given to enable us to calculate a more accurate intensity for all the lines of the band.

Spectra of the two gases, SO_2 and SO_3 , which are involved in the acid rain problem, have also been the subject of some studies. Many of the weaker transitions of SO_2 in the 450 to 600 cm^{-1} region have now been identified as due to the $^{34}\text{SO}_2$ species which comprises 4.2% of a normal sample. The low frequency ν_2 and ν_4 bands of SO_3 have also been studied and a complete set of constants have been determined that allow one to calculate the appearance of those bands with confidence.

Frequency Calibration Benchmarks

This laboratory has been involved in a collaboration on frequency calibration measurements with Joe Wells at the NIST/Boulder laboratory. New measurements on a number of bands of OCS have led to new frequency calibration data for the 490 to 3000 cm^{-1} region. By means of frequency measurements, nearly all the energy levels of OCS below 3000 cm^{-1} have now been tied to the cesium frequency standard with an uncertainty of ± 9 MHz (± 0.0003 cm^{-1}) or better.

New heterodyne measurements were also made on N_2O to provide improved accuracy for the frequency values for the ν_2 band in the 520 to 660 cm^{-1} region as well as to improve our knowledge of the lower energy levels of this molecule.

To fill a gap between the N_2O and OCS calibration data, the frequencies of a number of transitions of the strong ν_3 band of CS_2 were measured. By combining data on both $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$, which are easily seen in a low pressure sample, calibration tables were prepared for the 1460 to 1550 cm^{-1} region.

A major new input for the preparation of calibration tables is the new far-infrared heterodyne measurements that have been made on the high-J transitions in the rotational spectrum of OCS. The far-infrared measurements will give greater accuracy to our evaluation of the centrifugal distortion constants in the vibrational levels below about 1900 cm^{-1} .

E. Publications Resulting from NASA-sponsored Research 1988-1989

1. "Rotational Constants of the Lowest Torsional Component (OG) of the Ground State and Lowest Torsional Component (1G) of the First Excited Torsional State of Hydrogen Peroxide," W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, and J. W. Brault, J. Mol. Spectrosc. 127, 12 (1988).
2. "High-Resolution Measurements of the ν_2 Band of HNO_3 and the ν_3 Band of trans-HONO," A. G. Maki, J. Mol. Spectrosc. 127, 104 (1988).
3. "Heterodyne and FTS Measurements on the OCS Hot Bands near 1890 cm^{-1} ," A. G. Maki, W. B. Olson, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. 130, 69 (1988).
4. "Spectroscopic Constants for the ν_9 Infrared Band of HNO_3 ," A. Goldman, J. B. Burkholder, C. J. Howard, R. Escribano, and A. G. Maki, J. Mol. Spectrosc. 131, 195 (1988).
5. "Calibration Tables Covering the 1460 to 1550 cm^{-1} Region from Heterodyne Frequency Measurements on the ν_3 Bands of $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$," J. S. Wells, M. Scheider, and A. G. Maki, J. Mol. Spectrosc. 132, 422-428 (1988).
6. "Infrared Spectrum of the ν_6 , ν_7 , and ν_8 Bands of HNO_3 ," A. G. Maki and W. B. Olson, J. Mol. Spectrosc. 133, 171-181 (1989).

7. "Heterodyne Measurements on N_2O near 1635 cm^{-1} ," M. D. Vanek, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. 134, 154-158 (1989).
8. "Heterodyne Measurements on OCS near 1372 cm^{-1} ," M. Schneider, A. G. Maki, M. D. Vanek, and J. S. Wells, J. Mol. Spectrosc. 134, 349-353 (1989).
9. "Heterodyne Frequency and Fourier Transform Spectroscopy Measurements on OCS near 1700 cm^{-1} ," J. S. Wells, M. D. Vanek, and A. G. Maki, J. Mol. Spectrosc. 135, 84-88 (1989).
10. "Infrared Spectrum of the 1205 cm^{-1} band of HNO_3 ," A. G. Maki, J. Mol. Spectrosc. 136, 105-108 (1989).

Papers in Progress

1. "Frequency Measurements of High-J Rotational Transitions of OCS and N_2O ," M. D. Vanek, D. A. Jennings, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (in press).
2. "The ν_2 and ν_4 IR bands of SO_3 ," J. Ortigoso, R. Escribano, and A. G. Maki, (submitted to J. Mol. Spectrosc.).
3. "Calibration Tables Based on Frequency Measurements," A. G. Maki and J. S. Wells, (manuscript in preparation).

A. Title of Research.

Molecular Frequency Calibration Standards and Tunable Laser Spectroscopy in Support of Upper Atmospheric Research.

B. Investigators and Institutions.

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Martin Schneider from the Institut für Angewandte Physik, der Universität Bonn, Bonn West Germany was a NIST guest researcher in the Time and Frequency Division during portions of this period.

C. Abstract of Research Objectives.

The primary objective of this research is to provide reference tables (in the 0 to 3000 cm^{-1} region) of frequencies of molecular transitions (both transitions from the ground level and relevant hot band transitions are required to provide definitive signatures) along with other information such as relative intensities and lower energy levels. These values serve as frequency or wavenumber calibration points, not only for spectroscopic studies of molecules in the upper atmosphere, but also for the community of spectroscopists at large. The first step in the generation of these tables requires accurate heterodyne frequency measurements with a system comprised of tunable diode lasers (TDLs) and associated optics, a CO_2 laser frequency synthesizer, and CO lasers which serve as transfer oscillators. A second step in the generation of the reference tables involves fitting the data and predicting values for calibration tables from the newly determined constants.

D. Summary of Progress and Results.

Work (in the form of the two steps above) has continued on both carbonyl sulfide (OCS) and nitrous oxide (N_2O). This is part of an ongoing effort to bring a broad coverage calibration atlas (based primarily on these molecules) into fruition. Currently direct heterodyne frequency measurements are possible in our lab in the regions 860-1110 cm^{-1} (CO_2 laser coverage) and 1220 to 2080 cm^{-1} (CO laser coverage). Direct measurements were made on OCS in the 1850-1914 and 1650-1727 cm^{-1} regions [1,6]. Beyond a higher density of newly calibrated lines for definite signatures, the hot band measurements permitted calculated transitions in the regions 2508-2577 and 2695-2762 cm^{-1} [1] and 2915-2964 cm^{-1} [6]. The transfer oscillator technique was also extended for the first time into the 2080 cm^{-1} region, and new frequency measurement based calibration tables for the 1975-2090 cm^{-1} region will soon be available [12]. New OCS measurements at 1372 cm^{-1} also permitted accurate calculation outside of the region of direct measurements; a 488-557 cm^{-1} table is given in [8].

Current OCS fitting procedures call for a simultaneous fitting of all heterodyne plus other data made to date in order to obtain the best possible constants. Ref. [10] gives some results of measurements of high-J rotational transitions made on OCS (and N₂O) low lying levels. Similar work has been done on N₂O; measurements at 1635 cm⁻¹ yield tables for 519-661 cm⁻¹ [7], and hot band measurements at 930 cm⁻¹ permit a table covering 2725-2840 cm⁻¹ [11]. A gap in the coverage of OCS and N₂O in the 1400 cm⁻¹ region is partially covered by CS₂ (1460-1550 cm⁻¹) [3], and potentially by SO₂ (in progress, [14]) for the 1340-1400 cm⁻¹ region. CO transitions have now been determined by frequency measurements over the range 1250-2080 cm⁻¹ [4,9,13].

E. Journal Publications for 1988 and 1989 (References).

1. Heterodyne and FTS Measurements on the OCS Hot Bands Near 1890 cm⁻¹. A. G. Maki, W. B. Olson, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. 130, 69-80 (1988).
2. Improved Rotational Constants for HF, D. A. Jennings and J. S. Wells, J. Mol. Spectrosc. 130, 267-268 (1988).
3. Calibration Tables Covering the 1460 to 1550 cm⁻¹ Region from Heterodyne Frequency Measurements on the ν_3 Bands of ¹²CS₂ and ¹³CS₂, J. S. Wells, M. Schneider, and A. G. Maki, J. Mol. Spectrosc. 132, 422-428 (1988).
4. ¹²C¹⁶O Laser Frequency Tables for the 34.2 to 62.3 THz (1139 to 2079 cm⁻¹) Region, M. Schneider, K. M. Evenson, M. D. Vanek, D. A. Jennings, J. S. Wells, A. Stahn, and W. Urban, NBS Tech Note No. 1321 (1988).
5. Current Status of Calibration Frequencies for Tunable Diode Lasers from Heterodyne Frequency Measurements, J. S. Wells, M. D. Vanek, A. G. Maki, M. Schneider, and A. Hinz, (16 p) Monitoring of Gaseous Pollutants by Tunable Diode Lasers, D. Reidel Pub. Co. (1989).
6. Heterodyne Frequency and Fourier Transform Measurements on OCS near 1700 cm⁻¹, J. S. Wells, M. D. Vanek, and A. G. Maki, J. Mol. Spectrosc. 135, 84-88 (1989).
7. Heterodyne Measurements on Nitrous Oxide near 1635 cm⁻¹, M. D. Vanek, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. 134, 154-158 (1989).
8. Heterodyne Measurements on Carbonyl Sulfide near 1372 cm⁻¹, M. Schneider, A. G. Maki, M. D. Vanek and J. S. Wells, J. Mol. Spectrosc. 134, 349-353 (1989).
9. Heterodyne Frequency Measurements of ¹²C¹⁶O Laser Transitions, M. Schneider, K. M. Evenson, M. D. Vanek, D. A. Jennings, J. S. Wells, A. Stahn, and W. Urban, J. Mol. Spectrosc. 135, 197-206 (1989).
10. Frequency Measurements of High-J Rotational Transitions of OCS and N₂O, M. D. Vanek, D. A. Jennings, J. S. Wells and A. G. Maki, J. Mol. Spectrosc. (in press).
11. Heterodyne Frequency Measurements on N₂O near 930 cm⁻¹, A. G. Maki, J. S. Wells, and M. D. Vanek, J. Mol. Spectrosc. (in press).
12. Heterodyne Frequency Measurements of OCS near 2060 cm⁻¹, J. S. Wells, M. Schneider, and A. G. Maki, J. Mol. Spectrosc. (to be submitted).
13. Heterodyne Frequency Measurements of CO Laser Transitions near 4.9 μ m, M. Schneider, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (to be submitted).
14. Heterodyne Frequency Measurements on SO₂ near 1360 cm⁻¹, M. D. Vanek, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. (in progress).

A. TITLE OF RESEARCH TASK

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY
OF
MOLECULES OF ATMOSPHERIC IMPORTANCE

B. INVESTIGATORS AND INSTITUTIONS

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C. ABSTRACT OF RESEARCH OBJECTIVES

It has been demonstrated that remote sensing techniques based upon millimeter and submillimeter (mm/submm) technology can make important contributions to atmospheric science. The planning, execution, and interpretation of those experiments require a firm knowledge of the spectroscopic properties of atmospheric molecules. Our work is designed to support these atmospheric observations via contributions to the spectroscopic data base for the microwave through infrared spectral region. The work includes both the direct measurement of millimeter and submillimeter wave spectra of important atmospheric species and the calculation of synthetic spectra from these measurements. Results include line positions and linewidths in both the ground and excited vibrational states.

D. SUMMARY OF PROGRESS AND RESULTS

During this period we have carried out measurements of line positions, widths, and intensities in the millimeter, submillimeter, and far infrared spectral regions and have done theoretical calculations in support of these measurements. Species studied include HNO_3 , NO_2 , CF_2Cl_2 , HDO , HOOH , and N_2O_5 . Much of the work finished in this period is detailed in the "JOURNAL PUBLICATIONS" section below and can only be briefly summarized here. It includes a number of extensive mm/submm studies of the rotational structure of excited vibrational states. In addition to characterizing the mm/submm spectra of these excited vibrational states, it has been found that these studies also define much of the rotational structure of the infrared bands, thus making significant contributions to both the mm/submm and infrared data bases.

The N_2O_5 work (done in collaboration with B. P. Winnewisser and M. Winnewisser in Giessen, West Germany) was especially interesting. It was motivated by a need for better information at long wavelengths so that the usefulness of these spectral regions for remote sensing of N_2O_5 could be evaluated. This work included measurements of line positions, shapes, and intensities in the $25 - 350 \text{ cm}^{-1}$ region.

We have also carried out a number of studies of pressure broadening in these species. Because of the number of lines in the mm/submm, far infrared, and infrared for which the linewidths need to be known, we have placed emphasis on methods which will allow laboratory measurements on a subset of them to be used to provide reliable predictions of linewidths for many more lines. In addition, we have completed a new system designed for pressure broadening measurements in the region between 77 K and 500 K. Although this exceeds the temperature range necessary for direct atmospheric comparisons, we feel that this wide temperature capability is important for comparisons with theory so that theory and experiment can bootstrap one another to provide reliable spectroscopic information of wide applicability.

E. JOURNAL PUBLICATIONS

R. A. Booker, R. L. Crownover, F. C. De Lucia, and P. Helminger, "Millimeter and Submillimeter Wave Spectra of the ONO' Bending Mode (ν_7) in Nitric Acid," *J. Mol. Spectrosc.* **128**, 62 (1988).

T. M. Goyette, W. L. Ebenstein, F. C. De Lucia, and P. Helminger, "Pressure Broadening of the Millimeter and Submillimeter Wave Spectra of Nitric Acid by Oxygen and Nitrogen," *J. Mol. Spectrosc.* **128**, 108 (1988).

R. A. Booker, R. L. Crownover, F. C. De Lucia, and P. Helminger, "Millimeter and Submillimeter Wave Spectra of the NO' Stretching Mode (ν_6) in Nitric Acid," *J. Mol. Spectrosc.* **128**, 306 (1988).

F. C. De Lucia and S. Green, "Recent Advances in Pressure Broadening: Experiment and Theory," *J. Mol. Struct.* **190**, 435 (1988).

T. M. Goyette, W. L. Ebenstein, S. L. Shostak, F. C. De Lucia, and P. Helminger, "Pressure Broadening of NO₂, CF₂Cl₂, HDO, and HOOH by O₂ and N₂ in the Millimeter Wave Region," *J. Quant. Spectrosc. Radiat. Transfer* **40**, 129 (1988).

R. L. Crownover, R. A. Booker, F. C. De Lucia, and P. Helminger, "The Rotational Spectrum of Nitric Acid: The First Five Vibrational States," *J. Quant. Spectrosc. Radiat. Transfer* **40**, 39 (1988).

F. C. De Lucia, B. P. Winnewisser, M. Winnewisser, and G. Pawelke, "The Far-Infrared Spectrum of N₂O₅ in the Gas Phase," *J. Mol. Spectrosc.* **136**, 151 (1989).

T. M. Goyette and F. C. De Lucia, "The Millimeter and Submillimeter Wave Spectrum of the $\nu_8 + \nu_9$ State of HNO₃, submitted for publication.

T. M. Goyette, W. L. Ebenstein, S. L. Shostak, and F. C. De Lucia, "The Pressure Broadening of NO₂ in the Millimeter and Submillimeter Spectral Region," submitted for publication.

1989 NASA Research Summary

A. The Electronic Spectroscopy of HO₂ Radicals

B. Principal Investigator: James P. Reilly
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Starting Date: April 1989

C. Abstract

In recent preliminary experiments we have discovered an electronic absorption band of the hydroperoxyl radical in the visible spectral region. The goal of the proposed work is to complete the rotational analysis and vibronic assignment of this band and to probe nearby wavelength regions for evidence of other spectroscopic transitions that are part of this same system. Collisional relaxation studies are also being performed to verify that the OOH spectrum that we see derives from vibrationally unexcited radicals. This is significant if the observed absorption band is to be used in atmospheric monitoring.

D. Summary of Progress and Results

Last year we found that by introducing hydrogen peroxide vapor into a glass photoacoustic cell we were able to record an absorption spectrum of the transient free radical OOH. While the rotational structure of the observed band provided convincing proof that we had detected OOH, a vibronic assignment for the observed transition could not be made. Although the rotational structure was found to be describable by a room temperature Boltzmann distribution, whether or not the absorption took place from the (0,0,0) level of the ground electronic state was not absolutely clear.

In order to gather more information about the vibronic assignment of the observed transition, we are attempting to extend our spectral measurements to longer wavelengths. This is being pursued in two ways. First, since an excimer laser pumped dye laser is much easier to use in the near-infrared than is a CW ring laser, we are extending our photoacoustic technique to the pulsed laser domain. We have very recently recorded a spectrum of the highly forbidden $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ electronic transition of O₂ using the new approach. Second, we are planning to arrange to borrow an Argon ion laser pumped titanium sapphire laser from the Spectra Physics Corporation for a few days. We should be able to quickly reproduce the ring dye laser experiments and then obtain preliminary data at longer wavelengths. Unfortunately, these commercial lasers are in high demand and we will only have a few days to work with it.

As these experiments progress, we are continuing to work on our rotational structural analysis in order to obtain optimized rotational constants for the one complete spectral band that we have already observed. A simplex optimization code has been written to accomplish this and about 40 lines have thus far been definitely assigned.

Collisional Lineshapes and Molecular Beam Spectroscopy
of Atmospheric Molecules

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Collaborators: Gerald T. Fraser, NIST

L. Larrabee Strow, U. of Md., Balto. Co.
Josef M. Pliva, Penn State

Objectives:

The purposes of this program are to study collisional lineshapes and to obtain molecular beam spectra of various atmospheric molecules of interest to the NASA UARS (Upper Atmosphere Research Satellite), ATMOS (Atmospheric Trace Molecule Spectroscopy) and HALOE (Halogen Occultation Experiment) projects. The pressure broadenings, shifts and line profiles are required for quantitative monitoring of the distribution of contaminant gases and for temperature sounding of the atmosphere. Many of the molecular species of interest exhibit marked deviations in lineshape from the simple Lorentzian or Voigt profiles usually employed to model the spectral absorptions. A number of physical phenomena contribute to these lineshape distortions including collisional (Dicke) narrowing, speed-dependent collisional cross sections, non-impact (finite collision time) behavior, and collisional interferences (line coupling or line mixing). The precise measurement of these line profiles requires very high resolution infrared instrumentation such as the tunable difference-frequency-laser system and the color-center-laser photoacoustic spectrometer at NIST. Some of the heavier atmospheric molecules exhibit extremely dense, often strongly perturbed, spectra at normal atmospheric temperatures which have not been analyzed even with Doppler-limited resolution. In these cases molecular beam techniques can provide initial assignments due to sub-Doppler resolution and the considerable spectral simplification from the very low effective temperatures in an adiabatic expansion.

Summary of Progress:

Collisional Lineshapes:

Q-Branch Line Mixing: We have recorded the 2798 cm^{-1} band Q branch of N_2O and three Q-branches in the C-H stretch-bend combination region of HCCH using transmission spectroscopy with a difference-frequency laser system. The spectral profiles were examined from the Doppler limit at low pressures to the heavily overlapped regime at pressures approaching one atmosphere. The contours of these Q branches exhibit non-additive behavior in that they cannot be fit with a direct superposition of Lorentzian lines with the known intensities and positions of the components. Superposition deviations in the absorption constants are most evident near the band head and wings where most temperature sounding and monitoring is performed. These deviations arise from collisional line coupling when collisions can transfer intensity between overlapping lines in the spectra. Inelastic collisions that transfer population to states not involved in the overlapped transitions lead to normal

superposable broadening. Since the Q branches in linear molecules access only one vibrational "parity" (f level) component of doublet Π levels, we find that $f \leftrightarrow f$ conserving collisions result in line mixing while $f \leftrightarrow e$ contribute only broadening. Additional restrictions on the off-diagonal relaxation matrix elements have been imposed empirically to reduce the amount of line coupling observed, particularly for HCCH, which will require further theoretical justification and experimental verification.

Photoacoustic Measurement of Differential Broadening of the Λ Doublets of NO: In prior studies of the self and N_2 broadening of the overtone band of NO, we observed a small collision-induced asymmetry of the Λ doublets which exhibit equal widths and intensities under low-pressure Doppler-limited conditions. We have improved the precision and reliability of these measurements by using photoacoustic spectroscopy with a linear-scan-controlled color-center laser, which minimizes baseline channeling errors compared to the previous transmission spectra. The differential broadening has been observed in an Ar buffer gas to eliminate complications from rotational, vibrational and electronic resonances. The asymmetry is roughly proportional to J, reaching about 6% for $J=15.5$, and is seen in the P and R branches but not the Q branch. The anisotropy of the unpaired electron's Π orbital wavefunction in and out of the plane of rotation (Hund's case (b) admixture) appears to be responsible.

Molecular Beam Spectroscopy:

Molecular-Beam Spectroscopy of CHF_3 : The ν_1 C-H stretching fundamental band of fluoroform, CHF_3 (Freon 23), is strongly perturbed and its $T=295$ and 87 K Doppler-limited spectra, which we have previously recorded, have resisted analysis. We then recorded a subDoppler, $T \approx 4$ K spectrum using an optothermal (bolometer-detected molecules) molecular beam apparatus excited by a color-center laser. This has enabled us to assign the spectrum and identify the principal perturbations as anharmonic and Coriolis interactions with the A_1 and A_2 components of the bending combination, $\nu_4 + \nu_5 + \nu_6$. The global Fermi resonance with the C-H bending overtone, $2\nu_4$, is also under investigation.

Publications:

1. Q-Branch Line Mixing in N_2O : Effects of ℓ -type Doubling.
L.L. Strow and A.S. Pine, J. Chem. Phys. 89, 1427 (1988).
2. Doppler-Limited Spectra of the C-H Bending Overtone of Fluoroform.
A.S. Pine and J.M. Pliva, J. Mol. Spectrosc, 130, 431 (1988).
3. Molecular Beam Spectrum of the Highly Perturbed C-H Stretching Region of Fluoroform.
A.S. Pine, G.T. Fraser and J.M. Pliva, J. Chem. Phys. 89, 27270 (1988).
4. Photoacoustic Measurement of Differential Broadening of the Λ Doublets in $NO(X^2\Pi_{1/2}, v=2-0)$ by Ar.
A.S. Pine, J. Chem. Phys. 91, xxxx (1989).

Tunable Far Infrared Studies of Molecular Parameters in Support of Stratospheric Measurements

Investigators and Institutions:

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Abstract of Research Objectives:

The purpose of this research is to make precise, fully line-resolved measurements of molecular parameters that are necessary for the analysis of spectra obtained in far infrared field measurement programs. These measurements make it possible to accurately analyze the data from field measurements to obtain atmospheric concentration profiles of key trace gases involved in the ozone chemistry.

The research objectives include: measurements of pressure broadening of molecular lines of OH, O₂, O₃, HCl, and H₂O, their temperature dependences and, when possible, the pressure-induced frequency shifts of the lines; measurements of line positions of radical species, such as HO₂.

This research is done in collaboration with K. M. Evenson and D. A. Jennings, National Institute for Standards and Technology, Boulder, CO

Summary of Progress and Results:

Progress to date in this research includes the following studies:

OH Pressure broadening measurements have been made on the hyperfine-split OH lines at 3.551 THz, including: pressure broadening by He and H₂ as functions of temperature from 77 K to 300 K and; pressure broadening by N₂ and O₂ as functions of temperature from 210 K to 300 K. Pressure broadening of the 1.838 THz OH lines by the same gases has been measured at room temperature.

HO₂ The positions of 13 rotational lines of HO₂ have been measured between 2.5 to 5.9 THz, including transitions from levels with K_a as high as 5. A parameterized Hamiltonian is currently being fitted to the new measured positions to provide an improved set of molecular constants for HO₂.

HCl The pressure broadening and shifting of the 83.39 cm⁻¹ (2.500 THz) line of H³⁵Cl at room and stratospheric temperatures have been measured.

O₂ Air- and oxygen-broadening of the 61.32 and 117.87 cm⁻¹ O₂ rotational lines have been measured at stratospheric temperatures.

Publications are currently being prepared on OH, O₂, and HCl.

FAR INFRARED SPECTROSCOPY: ATMOSPHERIC PHYSICS

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ABSTRACT

Ultra high resolution far Infrared laser spectra of molecules of atmospheric importance yield accurate frequencies of their rotational transitions and accurate broadening coefficients. The frequencies are used to identify these species in the atmosphere, and the broadening coefficients are used in determining their absolute concentrations. Two different spectroscopic techniques are used: laser magnetic resonance (LMR) and tunable far infrared (TuFIR) spectroscopy.

PROGRESS AND RESULTS

Far infrared spectra of atmospheric molecules are used to identify species whose atmospheric emission spectra have been observed. Researchers at Harvard College Observatory and at Istituto di Ricerca Elettromagnetica CNR, Italy are making such measurements using high altitude balloon borne Fourier transform spectrometers. O_2 , OH, and HNO_3 spectra have previously been measured; during the past two years, CO, HCl, and HF (1), and HD (2) frequencies were published; and the publication on the HO_2 spectra is in preparation.

Line broadening coefficients have been determined for a number of different transitions of various molecules with various collisional partners. These coefficients are necessary to determine the absolute concentrations of the molecule from its emission spectra. The data is also used in determining the pointing direction of the telescopes used in taking the emission data. Previously, a few HCl and OH transitions were measured, and, now, an important O_2 transition broadening coefficient has been reported (3). Measurements of broadening of various transitions of OH, O_2 , and HCl have been completed and the publications are in preparation.

We plan to extend the spectral frequency measurements to other molecules and to measure the broadening coefficients of a number of molecules including temperature dependences of some.

Publications

1. Accurate Rotational Constants of CO, HCl, and HF: Spectral Standards for the 0.3 to 6 THz (10 to 200 cm^{-1} Region, I.G. Nolt, J.V. Radostitz, G. DiLonardo, K.M. Evenson, D.A. Jennings, K.R. Leopold, M.D. Vanek, L.R. Zink, A. Hinz, and K.V. Chance, J. of Mol. Spectrosc. 125, 274-287.
2. Frequency Measurement of the $J = 1 \leftarrow 0$ Rotational Transition of HD, K.M. Evenson, D.A. Jennings, J.M. Brown, L.R. Zink, K.R. Leopold, M.D. Vanek, and I.G. Nolt, submitted to Ast. Phy. J. Lett., 330, L135-6.
3. Air and Oxygen-Broadening Coefficients for the O_2 Rotational Line at 60.46 cm^{-1} , D. A. Jennings, K.M. Evenson, M.D. Vanek, I.G. Nolt, J.V. Radostitz, and K.V. Chance, Geophysical Research Lett. 14, 722-725.

A. Title: Laboratory Studies of Vibration-Rotation Lineshapes of Atmospheric Constituents

B. Investigator and Institution:

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University of Maryland Baltimore County

C. Abstract of Research Objectives

The purpose of this research is to improve our understanding of the spectra of atmospheric constituents important for satellite remote sensing. In particular, investigations that support the CLAES (Cryogenic Limb Array Etalon Spectrometer) and ISAMS (Improved Stratospheric and Mesospheric Sounder) instruments on UARS (Upper Atmosphere Research Satellite) are being pursued. One of the main goals of this work is to study the 791 cm^{-1} Q branch of CO_2 used by CLAES for temperature retrievals. Particular attention is being paid to the effects of line mixing on this Q branch and on other CO_2 bands. Most of the Q branch experimental studies are performed with a tunable diode laser spectrometer.

D. Summary of Progress and Results

A considerable number of spectra of the 791 cm^{-1} CO_2 Q branch used by CLAES for temperature and pressure sounding have been recorded using four different lasers. Spectra of the Q-branch from Q(2) through Q(28) over a wide pressure range were obtained as well as spectra of 70% of the R-branch lines between R(2) and R(32). These measurements show that the line strengths reported in the AFGL HITRAN database are too high by 17%. This difference is much larger than the 3% accuracies required for the CLAES experiment. These spectra also exhibit line mixing which can be accounted for with a scaling law approximation for rotational relaxation in CO_2 .

The line strengths in this band were determined from the diode laser spectra using a new method we developed for this work. Diode laser spectra at low frequencies (such as 791 cm^{-1}) can be severely broadened by the laser emission profile. We have found that the most accurate way to account for this instrument distortion is to use a modified equivalent width method that is described in the first journal publication listed below.

The development of line mixing models appropriate for atmospheric radiative transfer codes has continued. Methods to minimize numerical problems that arise when incorporating line mixing in standard radiative transfer codes have been developed and are being incorporated into GENLN2, the new atmospheric radiative transfer code developed by David Edwards at Oxford.

Curtis Rinsland (NASA/Langley) and I have observed line mixing in the 1932 cm^{-1} CO_2 Q branch in the SpaceLab 3 ATMOS spectra. This work represents the first test of my line mixing formalism at low temperatures.

Spectra of line mixing in a CO_2 Q branch over a wide temperature range (210K to 350K) have been recorded using our tunable diode laser spectrometer. We found that the simple scaling law model for line mixing successfully models the observed spectra over the complete temperature range. However, a different scaling law had to be used for each temperature. We are now trying to develop a single scaling law that is accurate over the complete temperature range.

Far wing CO_2 lineshapes are important for the ISAMS experiment on UARS. Previous attempts to compare experimentally observed far wing lineshapes to theory have failed due to the neglect of line mixing. This has stopped attempts to develop physically meaningful far wing lineshapes for atmospheric spectra. We have analyzed existing laboratory observations of far wing CO_2 lineshapes in the $4.3\text{ }\mu\text{m}$ R-branch of CO_2 and found that a reasonable physical model for the far wing lineshape is possible if line mixing is included.

Ab-initio calculations of line mixing are needed to put my phenomenological formulation of line mixing on firmer ground. Unfortunately, good intermolecular potentials (and computer codes) exist

only for linear molecule - atom collisions, so ab-initio calculations for $\text{CO}_2\text{-N}_2$ collisions are not possible at present. However, calculations of line mixing for $\text{CO}_2\text{-Ar,He}$ collisions are possible. I have recorded Q-branch spectra of CO_2 broadened by Ar and He in order to compare to ab-initio calculations by Sheldon Greene of NASA/Goddard Institute for Space Studies. His calculations agree very closely with my phenomenological scaling law calculations of line mixing for the $\text{CO}_2\text{-He}$ system. However, both calculations disagree significantly with the observed spectra in the wing of the Q branch for unknown reasons.

E. Journal Publications (1988-1989):

L. L. Strow and L. Zheng, **A Modified Equivalent-Width Technique for Diode-Laser Line Strength Measurements**, accepted for publication, J. Quant. Spectrosc. Rad. Trans., 1989.

C. P. Rinsland and L. L. Strow, **Line Mixing Effects in Solar Occultation Spectra of the Lower Stratosphere: Measurements and Comparisons with Calculations for the $1932\text{ CO}_2\text{ cm}^{-1}$ Q Branch**, Applied Optics, 28, 457-464, 1989.

L. L. Strow, **Line Mixing in Infrared Atmospheric Spectra**, Invited Paper, Modeling of the Atmosphere, Critical Reviews of Optical Science and Technology Series, Laurence S. Rothman, Editor, SPIE Vol. 928, 194-212, 1988.

L. L. Strow and A. S. Pine, **Q-Branch Line Mixing in N_2O : Effects of I-Type Doubling**, J. Chem. Physics, 89, 1427-1434 (1988).

L. L. Strow and D. Reuter, **The Effect of Line Mixing on Atmospheric Brightness Temperatures Near $15\text{ }\mu\text{m}$** , Applied Optics, 27, 872-878 (1988).

A. Title of Research Task

Laboratory Spectroscopic Measurements Relevant to Upper Atmospheric Research. (Grant-in-Aid No. NAGW-1238)

B. Investigator and Institution

Prasad Varanasi, Professor of Atmospheric Science, Institute for Atmospheric Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2300.

C. Abstract of Research Objectives

Infrared spectroscopic research that is being performed in our laboratory consists of measurements of absolute intensities and air-broadened half-widths of infrared spectral lines of atmospheric trace gases. The measurements are designed to yield data that are needed in the interpretation of many atmospheric remote sensing experiments conducted by NASA employing air-borne, balloon-borne, and satellite-borne infrared spectrometers. Our laboratory data are obtained at low temperatures relevant to the atmosphere using cryogenically cooled absorption cells and with the ultra-high spectral resolution ($\sim 10^{-4} \text{ cm}^{-1}$) of a tunable diode laser spectrometer.

D. Summary of Progress and Results

Intensity measurements were performed in the 720.8 cm^{-1} Q-branch of $^{12}\text{C}^{16}\text{O}_2$, since the $15 \mu\text{m}$ bands have been important in atmospheric spectroscopic studies such as remote sensing and temperature sounding of the atmosphere as well as in the study of the enhanced greenhouse effect brought about by the increase in the atmospheric concentration of CO_2 . Several of the past and proposed future satellite-borne temperature sounding experiments employ infrared spectral channels designed specifically to isolate the $15 \mu\text{m}$ lines of CO_2 . The accuracy of these sounders depends not only on the precision of the instruments employed but also on the reliability of the available spectroscopic database. Therefore, our purpose was to examine the validity of the currently adapted spectroscopic parameters, in particular, the intensities in the 720.8 cm^{-1} band. The accuracy of our results for the absolute intensities of the lines between 718.9499 cm^{-1} and 719.8319 cm^{-1} in the Q-branch and of the R(1) line at 722.3644 cm^{-1} to be about 98 % based upon the systematic errors and instrumental precision of our experiment.

Nitrous oxide is a trace constituent in the terrestrial atmosphere with an infrared-active fundamental band at $7.78 \mu\text{m}$. Since this strong absorption band is located in the so-called window region of the thermal infrared spectrum of the atmosphere, it is effective in enhancing the greenhouse effect and the resulting perturbation on the global climate. It is also important in atmospheric chemistry involving nitrogen, especially, in the production of odd nitrogen species of NO_x which are involved in the catalytic cycles that destroy O_3 directly. N_2O is recognized as the major source of NO_x in the stratosphere. Because $^{14}\text{N}_2^{16}\text{O}$ is produced in the troposphere and is destroyed in the stratosphere, it serves as a dynamical tracer of the motion of tropospheric air into the lower stratosphere. On account of this distinction, several studies of this molecule were featured in the 1987 Airborne Antarctic Ozone Experiment. The correlation between O_3 and N_2O as well as the relationship between CN and N_2O has also been studied as an important aspect of the airborne measurements that were performed on the so-called Ozone Hole in Antarctica. The thermal infrared lines of $^{14}\text{N}_2^{16}\text{O}$ have also been assigned special significance in the remote sensing of the Antarctic stratosphere with airborne Fourier transform spectrometers. In all of the above applications, accurate knowledge of the absolute intensities of the spectral lines in the ν_1 -fundamental band of $^{14}\text{N}_2^{16}\text{O}$ has become necessary. Interpretation of the N_2O spectra obtained with the airborne spectrometers also requires data on the air-broadened half-widths at low temperatures relevant to the Antarctic stratosphere, in which the temperatures can be as low as 190 K. The above stated applications point toward the need for laboratory data on the intensities and air-broadened half-widths of rotational lines in the ν_1 -fundamental of $^{14}\text{N}_2\text{O}$ and their temperature dependence at temperatures relevant to the terrestrial atmosphere. Therefore, we have performed measurements on several lines between 1240 and 1280 cm^{-1} using our tunable diode laser spectrometer. Line intensities have been determined along with N_2 -, O_2 -, and air-broadened line widths at several temperatures between 150 and 296 K. The values of the exponent n which describes the variation of the line width with temperature were found to be practically identical in N_2 -broadening and O_2 -broadening.

Laboratory data on the air-broadened halfwidths of spectral lines in the ν_4 -fundamental band of $^{12}\text{CH}_4$ at $7.66 \mu\text{m}$ and on their variation with temperature are necessary in the analysis of the thermal infrared spectrum of the atmosphere. We have, therefore, measured at several temperatures between 100 and 296 K the intensities and half-widths of P(5), P(6) and P(9) multiplets located between 1240 and 1280 cm^{-1} in broadening by N_2 , O_2 , Ar, and air. The temperature dependence and the relative magnitudes of the line widths of the A, E, F species of rotational lines were examined for each of the broadening cases.

We consider the present set of low temperature measurements on the lines of CH_4 and N_2O not only to be the most accurate to come out of our laboratory to date, but also, to the best of our knowledge, to be the first ever measured at low

temperatures employing the ultra-high spectral resolution ($\sim 10^{-4} \text{ cm}^{-1}$) of a tunable diode laser spectrometer. In view of the important role the spectral lines of $^{13}\text{CH}_4$ assume in remote sensing of the atmosphere, we have also measured the intensities and collision-broadened line widths in the ν_4 -fundamental band of $^{13}\text{CH}_4$ at 295 K. Ar, N_2 , O_2 , and air were chosen as the broadening gases.

Determination of the abundance of CH_3D in the atmosphere by analysing the observed spectra requires accurate laboratory data on the absolute intensities and air-broadened half-widths of the lines of CH_3D at temperatures that are relevant to the atmosphere. Therefore, we have measured at several temperatures between 100 and 296 K the intensities and half-widths of several multiplets in the ν_3 and ν_6 fundamentals of $^{12}\text{CH}_3\text{D}$. The temperature dependence of intensities and of half-widths of lines in N_2 -, O_2 -, Ar-, air-broadening has been determined.

We have also measured the pressure-induced shifts of several lines of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$ and $^{14}\text{N}_2^{16}\text{O}$ located between 1265 and 1350 cm^{-1} and of their temperature dependence, which we are the first ever to have measured.

We have recently completed measurements of the spectral transmittance of CF_2Cl_2 and CFCl_3 using ultra-high spectral resolution of the diode laser spectrometer and the moderate-resolution of a grating spectrometer at several temperatures between 200 and 296 K. We have determined accurately the temperature dependence of the absorption coefficient in the important thermal infrared bands of these two CFCs. These measurements are also first of their kind.

E. Journal Publications and a Ph.D. Dissertation

Varanasi, P. and Chudamani, S. : Measurement of Pressure-Induced Shifts of Infrared lines with a Tunable Diode Laser. *JQSRT* **41**, 173-176, 1989.

Varanasi, P. and Chudamani, S. : Absolute Intensity Measurements in the ν_4 - Fundamental Band of $^{12}\text{CH}_4$ at Planetary Atmospheric Temperatures. *JQSRT*, **41**, 345-349, 1989.

Varanasi, P. and Chudamani, S. : Measurements of Collision-Broadened Line Widths in the ν_4 - Fundamental Band of $^{12}\text{CH}_4$ at Low Temperatures. *JQSRT*, **41**, 335-343, 1989.

Varanasi, P. and Chudamani, S. : Tunable Diode Laser Measurements of line widths in the ν_1 - Fundamental Band of $^{14}\text{N}_2^{16}\text{O}$ at atmospheric temperatures. *JQSRT*, **41**, 351-357, 1989.

Varanasi, P. and Chudamani, S. : Line Strength Measurements in the ν_1 - Fundamental Band of $^{14}\text{N}_2^{16}\text{O}$ using a Tunable Diode Laser. *JQSRT*, **41**, 359-362, 1989.

Varanasi, P. and Chudamani, S. : Line Intensity Measurements in the ν_3 - and ν_6 - Fundamental Bands of $^{12}\text{CH}_3\text{D}$ at Low Temperatures Relevant to Planetary Atmospheric Observations. *J. Mol. Spectrosc.*, **134**, 440-444, 1989.

Varanasi, P. and Chudamani, S. : Linewidth Measurements in the Thermal Infrared Bands of $^{12}\text{CH}_3\text{D}$ at Planetary Atmospheric Temperatures. *Appl. Opt.* **28**, 2119-2122, 1989.

Varanasi, P. and Chudamani, S. : Measurements of Collision-broadened Line Widths in the $7.66 \mu\text{m}$ Band of $^{12}\text{CH}_4$ at Temperatures Relevant to the Atmosphere. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Intensity and Line Width Measurements in the ν_4 - Fundamental Band of $^{13}\text{CH}_4$. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Infrared Spectroscopic Measurements on Atmospheric Trace Gases at Relevant Temperatures. Invited Contribution in *IRS 88 : Current Problems in Atmospheric Radiation*. J. LeNoble and J. F. Geleyn, Eds., A. Deepak Publishing, 392-397, 1989.

Varanasi, P. and Chudamani, S.: The Temperature Dependence of Lineshifts, Linewidths and Line Intensities of Methane at Low Temperatures. *JQSRT* (in press).

Varanasi, P. and Chudamani, S. : Intensity Measurements in the 720.8 cm^{-1} Q-Branch of $^{12}\text{C}^{16}\text{O}_2$. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Measurements of the Spectral Absorption Coefficient in the Thermal Infrared Bands of CFC-11 and CFC-12 at Low Temperatures. *JQSRT* (submitted for publication).

Kratz, D. P. and Varanasi, P. : A Study of the Radiative Effects of CFCl_3 and CF_2Cl_2 . *J. Geophys. Res.* (submitted for publication).

Chudamani, S. : *Infrared Spectroscopic Measurements on Planetary Atmospheric Gases*. Dissertation submitted for the Ph. D degree in Atmospheric Sciences, State University of New York at Stony Brook, May 1989.

NASA Upper Atmosphere Research Program

RESEARCH SUMMARY 1988-1989

A. TITLE OF RESEARCH TASK

"A Facility for High Resolution Spectroscopy: Laboratory and Ground Based Observations in Support of Upper Atmospheric Research"

B. INVESTIGATORS AND INSTITUTIONS

Principal Investigator: J.W. Brault (National Solar Observatory)

Visiting Investigators:

Jet Propulsion Laboratory	Langley Research Center	Goddard Space Flight Center
L. R. Brown	C. Rinsland	J. J. Hillman
E. Cohen	M. A. H. Smith	D. E. Jennings
J. S. Margolis		T. Kostiuik
H. Pickett		
R. Poynter		
R. Toth		

C. ABSTRACT OF RESEARCH OBJECTIVES

This research task consists of operating a *facility* for making spectroscopic observations in support of upper atmospheric research. The facility responds to the needs and interests of the visiting investigators. Therefore, the research objectives are not predetermined except in broad outline. The emphasis is on studies that take advantage of the particular strengths of the Fourier transform spectrometer on Kitt Peak: high spectral resolution combined with wide spectral range and low noise.

D. SUMMARY OF PROGRESS, RESULTS AND PROPOSED WORK

During 1988 and 1989, eight sessions with the Kitt Peak FTS were scheduled by the laboratory spectroscopy group at NASA Langley Research Center. The Langley group has used the McMath FTS to record numerous high-quality spectra of methane and several of its isotopes in the 2.5 to 5 μm region and in the 6 to 8 μm region. These spectra are being analyzed along with similar methane spectra recorded in previous years to determine N_2 -, O_2 -, Ar-, and air-broadening coefficients and pressure-induced line shifts for a large number of absorption lines belonging to several different vibration-rotation bands of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{CH}_3\text{D}$. Results for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in the 6 to 8 μm region have been published and have already been applied in analysis of atmospheric data.

Continuing analysis of ozone absorption spectra recorded by the Langley group in 1984, 1985 and 1987 has resulted in improved line positions, intensities, and assignments in the 3 to 15 μm region. Analysis is also in progress to determine N_2 - and air-broadening coefficients and pressure-induced line shifts for lines in the 3.6 μm region, and self-broadening coefficients for lines in the 5 to 15 μm region.

A series of atmospheric solar absorption spectra were recorded using the McMath telescope and FTS in May 1988 and in November-December 1988, and a single spectrum was

recorded in May 1989. These spectra are being analyzed along with similar spectra previously recorded at the McMath since 1980 to obtain total column amounts of atmospheric trace species such as HF and CFCs to determine trends of these species amounts with time.

In FY89 Goddard Space Flight Center used the NSO FTS on two occasions. In January Fox, Jennings, Plymate, and Wagner recorded spectra of the 9 μm band of methane broadened by N_2 , O_2 , He, H_2 , Ar, CO, Ne, Kr, and Xe. The spectra were used to study the line widths and shifts induced in methane by these gases. Results were presented at the Spring APS meeting in Baltimore.

In May Jennings, Hillman, and Reuter recorded spectra of several gases at low temperature (160-180K). These included acetylene, propane, and N_2O . These were broadened by N_2 , H_2 , and He. Data is being analyzed at present.

F. JOURNAL PUBLICATIONS

Flaud, J. -M., C. Camy Peyret, J. W. Brault, C. P. Rinsland, and D. Cariolle, Nighttime and Daytime Variation of Atmospheric NO_2 From Ground-Based Infrared Measurements, *Geo. Phys. Res. Lett.*, 15, 261-264 (1988).

Flaud, J. -M., C. Camy Peyret, A. N'Gom, V. Malathy Devi, C. P. Rinsland, and M. A. H. Smith, The ν_2 Bands of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$: Line Positions and Intensities, *J. Mol. Spectrosc.*, 133, 217-223 (1989).

Fox, K., D. E. Jennings, E. A. Stern and R. Hubbard, Measurements of Argon, Helium and Hydrogen N_2 -Broadened Widths of Methane Lines Near 9000 cm^{-1} , *J. QSRT.*, 39, 473 (1988).

Fox, K., D. E. Jennings, Spectral Shifts of Methane Lines in Collisions With Hydrogen, Helium, Nitrogen, and Argon, *J. QSRT.*, 42, 201-206 (1989).

Malathy Devi, V., D. C. Benner, M. A. H. Smith, and C. P. Rinsland, Measurements of Air-, N_2 -, and O_2 - Broadened Halfwidths and Pressure-Induced Line Shifts in the ν_3 Band of $^{13}\text{CH}_4$, Manuscript submitted to *Appl. Opt.* (1989).

Margolis, J. S., Measured Line Positions and Strengths of Methane Between 5500 and 6180 cm^{-1} , *Appl. Opt.*, 27, 4038 (1988).

Margolis, J. S., Imperical Values of Ground State Energies for Methane Transitions Between 5500 and 6150 cm^{-1} , Manuscript submitted to *Appl. Opt.* (1989).

Rinsland, C. P., M. A. H. Smith, J.-M. Flaud, C. Camy-Peyret, and V. Malathy Devi, Line Positions and Intensities of the $2\nu_3$, $\nu_1+\nu_3$, and $2\nu_1$ Bands of $^{16}\text{O}_3$, *J. Mol. Spectrosc.*, 130, 204-212 (1988).

Rinsland, C. P., D. W. Johnson, A. Goldman, and J. S. Levine, Evidence for a Decline in the Atmospheric Accumulation Rate of CHClF_2 (CFC-22), *Nature*, 337, 535-537 (1989).

Rinsland, C. P., V. Malathy Devi, M. A. H. Smith, and D. C. Benner, Measurements of Argon-Broadened Lorentz Width and Pressure-Induced Line Shift Coefficients in the ν_4 Band of $^{12}\text{CH}_4$, *Appl. Opt.*, 28, 2111-2118 (1989).

Smith, M. A. H., C. P. Rinsland, V. Malathy Devi, J. -M. Flaud, C. Camy-Peyret, and A. Barbe, The 3.6 μm Region of Ozone: Line Positions and Intensities, Manuscript submitted to *Appl. Opt.* (1989).

Task Summary, August 1989

A. Title: Calibration Facilities for NASA Payloads at SURF

B. Principle Investigator: Robert P. Madden

Institution: U. S. Department of Commerce
National Institute of Standards and Technology
Radiation Physics Division
Gaithersburg, MD 20899

C. Abstract of Research Objectives:

It is critically important to have a common VUV radiometric base for the wide range of scientific missions being carried out by rocket, by satellite, and on the space shuttle. It has been demonstrated that this can be achieved utilizing the NASA Spectrometer Calibration Facility beamline at SURFII, the Synchrotron Ultraviolet Radiation Facility at the National Institute of Standards and Technology. This beamline, with its large spectrometer calibration chamber, utilizes the calculable nature of synchrotron radiation to calibrate a wide range of spectrometer and photometer systems, thereby serving as a common radiometric base. The accuracy of this calibration source has been thoroughly documented and is adequate to this task.

D. Summary of Progress and Results:

The NASA/SURF Spectrometer Calibration Facility was solidly booked during 1988 and 1989. In 1988, users included: J. Mentall (three times), GSFC (rocket spectrometers); W. Neupert (twice), GSFC (grating calibrations); G. Rottman/T. Woods (twice), LASP (UARS-SOLSTICE); P. Jelinsky, SSL (EUV Explorer); M. VanHoosier (twice), NRL (UARS-SUSIM); D. Judge, USC-SSC (EUV Spectrometer); T. Woods, LASP (EUV Spectrometer). In 1989, all of the above again performed calibrations using the facility. In all, some 29 NASA-related instrument calibrations were performed in 88-89.

SURF II was improved during this period. Maximum currents were increased from 221mA to 300mA, average currents were similarly improved, and the lifetime of the beam was increased by over 40%. New buffer amplifiers were designed, built, and installed on all beam lines to improve beam current monitoring.

Improvements to the Spectrometer Calibration Facility included adding three new higher capacity cryopumps to the Large Spectrometer Calibration Chamber and its bellows, two being supplied by the Naval Research Laboratory. A radiant heating system for the Large Spectrometer Calibration Chamber was implemented, and a new computer was provided for the on-site calculation of all fluxes in all geometries used by the calibration users. A new cryopump was installed at the 11m calibration station which has significantly decreased the time required for calibration at both the 11m station and in the Large Spectrometer Calibration Chamber. The gimbals drive return spring system was redesigned, the new system operated successfully in 1989, and the data

transmission rate for this drive system was speeded up by a factor of four. The hydraulic drive system for motion of the Large Spectrometer Chamber was completely overhauled, and a new computer to drive this system and the pitch and yaw motions of the internal gimbals will be installed by the end of the contract period.

E. Journal Publications:

Furst, M. L. and Madden, R.P., "Synchrotron Ultraviolet Radiation Facility (SURF II) Radiometric Instrumentation Calibration Facility," submitted for publication, 1988.

Lean, J. L., Kostkowski, H. J., Saunders, R. D., and Hughey, L. R., "Comparison of the NBS SURF and Argon Mini-Arc Irradiance Standards at 214 nm," *Applied Optics* 28, 3246 (1989).

P. Jelinsky, S.R. Jelinsky, A. Miller, J. Vallerger, R.S. Malina, "Synchrotron Radiation Calibration of EUVE Variable Line Spaced Diffraction Gratings at the NBS SURF II Facility", *SPIE Proceedings*, Vol. 982 (1988).

T. N. Woods and G. J. Rottman, "Solar EUV Irradiance Derived from Rocket Experiments on 10 Nov. 1988", submitted to *J. Geophysics Research* (Feb. 1989).

R. P. Madden, "News from SURF", an article published in *Synchrotron Radiation News*, March/April 89.

Additional talks given during this period include:

L. R. Hughey, "Record Capture and Acceleration Efficiency in the SURF-II 300 MeV Circular Storage Ring", an invited paper presented at the Accelerator Conference, Chicago (1989).

R. P. Madden, "UV-VUV Radiometry at NIST", an invited paper presented at the Committee on Optical Radiation Measurements (CORM) meeting, Gaithersburg (1989).

R. P. Madden, L. R. Hughey, A. Hamilton, and M. L. Furst, "SURF II - Progress and Opportunities" a poster paper presented at the U.S. Conference on Synchrotron Radiation Instrumentation, Berkeley, 1989.

J. Lean, "Solar Emission Variation Measurements and Interpretation", a NIST seminar, Gaithersburg (1989).

Analysis of Atmospheric Spectra for Trace Gases

Investigators and Institutions

P.I.: Curtis P. Rinsland, NASA Langley Research Center
 Co.-I's: Dr. Robert K. Seals, Jr., NASA Langley Research Center
 Dr. Mary Ann H. Smith, NASA Langley Research Center
 Dr. Aaron Goldman, University of Denver
 Dr. David G. Murcray, University of Denver
 Dr. Frank J. Murcray, University of Denver

Abstract of Research Objectives

The objective of this work is the comprehensive analysis of high-resolution atmospheric spectra recorded in the middle-infrared region to obtain simultaneous measurements of coupled parameters (gas concentrations of key trace constituents, total column amounts, pressure, and temperature) in the stratosphere and upper troposphere. Solar absorption spectra recorded at 0.002 and 0.02 cm^{-1} resolutions with the University of Denver group's balloon-borne, aircraft-borne, and ground-based interferometers and 0.005 to 0.01 cm^{-1} resolution solar spectra from Kitt Peak are used in the analyses.

Summary of Progress and Results

The major recent focus of this work has been the analysis of the very high (0.002 to 0.003 cm^{-1} FWHM) resolution stratospheric solar spectra recorded during three recent balloon flights. The spectra reveal many new features of several important trace gases, such as HNO_3 and COF_2 , as well as new details concerning the absorptions by ClONO_2 and HO_2NO_2 . Comparison of the new spectra with line-by-line simulations shows that previous spectral line parameters are often inadequate, and that new analysis of high resolution laboratory and atmospheric spectra and improved theoretical calculations will be required for many bands. Preliminary versions of several sets of improved line parameters have been developed and compared with the balloon-borne spectra. A laboratory analysis of the ν_6 band of COF_2 has been completed. Isotopic ratios of $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ relative to normal ozone have been measured based on recent improvements in ozone line parameters in the 10- μm region. Normalized to standard terrestrial isotopic ratios in ozone, both forms of heavy ozone are enriched above 37 km altitude with about a factor of two larger enhancement in $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ than $^{16}\text{O}^{18}\text{O}^{16}\text{O}$.

In preparation for the Network for the Detection of Stratospheric Change, 0.02- cm^{-1} resolution solar spectra recorded at Mauna Loa have been analyzed. Simultaneous total columns have been determined for 13 atmospheric gases, and the daytime diurnal variations of the NO and NO_2 total columns have been measured. The results indicate that Mauna Loa is a favorable site for infrared monitoring of atmospheric gases.

Analysis of the Kitt Peak ground-based solar spectra has continued. A series of 19 spectra recorded during the night using the Moon or during the day using the Sun as a source have been used to measure the daytime and nighttime variation of the NO_2 total column. A continuous increase is observed during the day (lifetime about 10.4 hours) followed by a rather rapid decrease during the night. At sunrise the NO_2 total column drops by about a factor of three. The measurements have been compared with values calculated with a 1-D diurnal photochemical model. Spectra recorded between December 1980 and May 1988 show that the CHClF_2 (CFC-22) total column increased at an average annual exponential rate of $7.8\% \pm 1.0\%$ (2σ). Compared with other atmospheric data, these

measurements indicate that CFC-22 is increasing at a more rapid rate than either CFC-11 or CFC-12, the two most abundant chlorofluorocarbons, but that the rate of CFC-22 increase is likely to have declined over the past few years. A systematic discrepancy between the absolute values of infrared and in situ CFC-22 measurements is noted.

Journal Publications (1988-1989)

1. Rinsland, C. P., A. Goldman, F. J. Murcray, F. H. Murcray, D. G. Murcray, and J. S. Levine: Infrared Measurements of Increased CF_2Cl_2 (CFC-12) Absorption Above the South Pole, Appl. Opt. 27, 627-630, 1988.
2. Flaud, J.-M., C. Camy-Peyret, J. W. Brault, C. P. Rinsland, and D. Cariolle: Nighttime and Daytime Variation of Atmospheric NO_2 from Ground-Based Infrared Measurements, Geophys. Res. Lett. 15, 261-264, 1988.
3. Goldman, A., F. J. Murcray, F. H. Murcray, D. G. Murcray, and C. P. Rinsland: Measurements of Several Atmospheric Gases Above the South Pole in December 1986 from High Resolution 3- to 4- μm Solar Spectra, J. Geophys. Res. 93, 7069-7074, 1988.
4. Rinsland, C. P., A. Goldman, F. J. Murcray, F. H. Murcray, and D. G. Murcray: Infrared Measurements of Atmospheric Gases Above Mauna Loa, Hawaii, in February 1987, J. Geophys. Res. 93, 12607-12626, 1988.
5. Goldman, A., F. J. Murcray, F. H. Murcray, D. G. Murcray, and C. P. Rinsland: Quantification of Several Atmospheric Gases from High Resolution Infrared Solar Spectra Obtained at the South Pole in 1980 and 1986, Mikrochim. Acta (Wien) 2, 409-415 (1988).
6. Rinsland, C. P., D. W. Johnson, A. Goldman, and J. S. Levine: Evidence for a Decline in the Atmospheric Accumulation Rate of CHClF_2 (CFC-22), Nature 337, 535-537 (1989).
7. Murcray, F. J., A. Matthews, A. Goldman, P. Johnston, and C. P. Rinsland: NH_3 Column Abundances over Lauder, New Zealand, J. Geophys. Res. 94, 2235-2238, 1989.
8. Goldman, A., F. J. Murcray, D. G. Murcray, J. J. Kusters, C. P. Rinsland, J.-M. Flaud, C. Camy-Peyret, and A. Barbe: Isotopic Abundances of Stratospheric Ozone from Balloon-Borne High Resolution Infrared Solar Spectra, J. Geophys. Res. 94, 8467-8473, 1989.
9. Goldman, A., F. J. Murcray, R. D. Blatherwick, J. J. Kusters, F. H. Murcray, D. G. Murcray, and C. P. Rinsland: New Spectral Features of Stratospheric Trace Gases Identified from High Resolution Infrared Balloon-Borne and Laboratory Spectra, J. Geophys. Res., in press.
10. Goldman, A., C. P. Rinsland, R. D. Blatherwick, and F. S. Bonomo: Spectroscopic Line Parameters for the ν_6 Band of Carbonyl Fluoride (COF_2), submitted to Appl. Opt.
11. Flaud, J.-M., C. Camy-Peyret, C. P. Rinsland, V. Malaty Devi, M. A. H. Smith, and A. Goldman: Improved Line Parameters for Ozone Bands in the 10 μm Spectral Region, submitted to Appl. Opt.

III. THEORETICAL STUDIES

- A. GLOBAL MODELLING OF STRATOSPHERIC CHEMISTRY
- B. MODELLING PHOTOCHEMICAL PROCESSES
- C. STRATOSPHERIC DYNAMICS

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A. GLOBAL MODELLING OF STRATOSPHERIC CHEMISTRY

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A. Zonally-averaged Model of Dynamics, Chemistry and Radiation for the Atmosphere

B. Principle Investigators : Nien-Dak Sze and Malcolm Ko
Co-investigators : Arthur Y. Hou, Jose M. Rodriguez, Hans-R. Schneider and Debra K. Weisenstein
Atmospheric and Environmental Research Inc., 840, Memorial Drive, Cambridge, MA 02139

C. Abstract of Research Objective

The overall goal of the project is to obtain an understanding of the processes that control the distribution and abundance of stratospheric ozone and its sensitivity to either natural or anthropogenic influences. The scientific objectives, which are designed around the two-dimensional zonal mean (2-D) modeling capability at AER, are :

- To assess the limitation of 2-D models, to refine and enhance our current (2-D) modeling capabilities and understanding of the stratosphere through model simulations and validation of model results using observed data.
- To develop an interactive 2-D model with interactive chemistry, dynamics and radiation.
- To assess the susceptibility of stratospheric ozone to natural and anthropogenic perturbations.
- To study the processes that give rise to the Antarctic Ozone Hole and assess their global impact.

D. Summary of Progress and Results

Ozone Budget

We used result from the 2-D model to clarify the roles of chemistry and transport in determining the concentration of O_3 in the 2-D model (Ko et al, 1989). We found that at the tropical lower stratosphere, the concentration of O_3 is determined by a balance between chemical production and transport out of the region. At high latitudes, the balance is between local chemical removal and transport into the region. Our study help to explain the response of model ozone to chemical perturbation and clarify the limitation of 1-D model results.

Assessment Calculations and Ozone Depletion Potentials

The calculated O_3 behavior in the future atmosphere from our assessment calculations were used in a study to examine the effect of redistribution of O_3 on climate (Wang et al, 1989). We performed a number of assessment calculations and provided inputs for the preparation of several reports including the NASA Reference Publication report 1208, "Present State of Knowledge of the Upper Atmosphere 1988 : An Assessment Report" and the UNEP/WMO report. We also used the 2-D model to calculate the Ozone Depletion Potential of a number of CFC substitutes and examined how the calculated values are affected by the transport parameters in the model.

Interactive Model and Dynamics

The interactive model is now operational. We have used the version with simplified chemistry to study the model sensitivity to Kyy (Schneider et al 1989) and the feedback effects from change in O_3 . Our model simulations showed that the temperature and dynamics feedback from change in local heating

could compensate for about 1/6 of the calculated O₃ decrease. The version of the model with full chemistry has been used to simulate the present day atmosphere and perform a number of steady state assessment calculations. The emphasis of the work is related to our theoretic study that clarify their role of Kyy in controlling the diabatic circulation (Hou and Ko, 1989).

Antarctic Ozone

Part of 1988 was spent in the analysis of the data from the Airborne Antarctic Ozone Experiment. Analysis of the data resulted in three publications that discussed the effect on global O₃ content from export of O₃-poor air from the vortex, the so-called dilution effect (Sze et al, 1989), the comparison of simulated trace gas distributions in the vortex with the AAOE observations (Rodriguez et al, 1989) and the decadal trend of the ozone behavior in the polar vortex (Ko et al, 1989).

E. Journal Publications

Rodriguez, J.M., M. K. W. Ko, and N. D. Sze (1988) Antarctic chlorine chemistry: possible global implications. Geophys. Res. Lett., 15, 257-260.

Hou, A.Y., and M. K. W. Ko (1989) Ageostrophic effects on the stratospheric residual circulation and tracer distributions. J. Atmos. Sci., 46, 1396-1406.

Schneider, H. R., M. K. W. Ko, N. D. Sze, G.-Y. Shi, and W.-C. Wang (1989) An evaluation of the role of eddy diffusion in stratospheric interactive 2-D models. J. Atmos. Sci., 46, 2079-2093.

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Wang, W.-C., G. Molnar, M. K. W. Ko, S. Goldenberg, and N. D. Sze (1989) Atmospheric trace gases and global climate: a seasonal model study. Tellus, in press.

Ko, M. K. W., J. M. Rodriguez, N. D. Sze, M. H. Profitt, W. L. Starr, A. Krueger, E. V. Browell, and M. P. McCormick (1989) Implications of AAOE observations for proposed chemical explanations of the seasonal and interannual behavior of Antarctic ozone. To appear in J. Geophys. Res.

Rodriguez J. M., M. K. W. Ko, N. D. Sze, S. D. Pierce, J. G. Anderson, D. W. Fahey, K. Kelly, C. B. Farmer, G. C. Toon, M. T. Coffey, L. E. Heidt, W. G. Mankin, K. R. Chan, W. L. Starr, J. F. Vedder, and M. P. McCormick (1989) Nitrogen and halogen species in the spring Antarctic stratosphere: comparison of models and AAOE observations. To appear in J. Geophys. Res.

Sze, N. D., M. K. W. Ko, D. K. Weisenstein, and J. M. Rodriguez (1989) Antarctic ozone hole: possible implications for ozone trends in the Southern hemisphere. To appear in J. Geophys. Res.

A. Acquisition and Utilization of Archived Satellite Data from the NASA Upper Atmospheric Research Program : Validation and Enhancement of a Two-dimensional Zonal-mean Model

B. Principle Investigators : Malcolm K. Ko and Nien-Dak Sze
Co-investigator : Arthur Y. Hou, Hans-R. Schneider and Debra K. Weisenstein
Atmospheric and Environmental Research Inc., 840, Memorial Drive, Cambridge, MA 02139

C. Abstract of Research Objective

The objective of the program is to acquire satellite data from the NASA Upper Atmosphere Research Program and to organise them in a form that is suitable for use in support of the two-dimensional modeling work at AER.

D. Summary of Progress and Results

Acquisition of Data

We have acquired and organised five data sets. These are the BUUV O₃ data; the SBUV O₃ data; the TOMS O₃ data; the LIMS data on temperature, O₃, NO₂, H₂O, HNO₃ and geopotential height; and the SAMS data on N₂O and CH₄. The data were interpolated into the AER model grid and processed that they are suitable for use as input for model studies and for comparison with model results.

Calculation of Diabatic Circulation Using Observed Temperature and O₃

The zonal-mean O₃ mixing ratio from SBUV was used together with the observed temperature from NMC to obtain the heating rate using the AER radiation code. A seasonal zonal-mean circulation was calculated from the diabatic heating rates.

Interannual Variation of Ozone

Using the O₃ concentrations and observed monthly mean temperature from NMC for the four year period (1978-1982), radiative heating rates were computed for each month of the four years. The circulations diagnosed from the heating rates were used in the 2-D chemistry-transport model to calculate the O₃ behavior. The model calculated inter-annual fluctuations was compared with the observation. Our model calculation suggested that the observed inter-annual variability in O₃ is a response to fluctuations in the transport circulation in the lower stratosphere. Furthermore, the year-to-year variations in the circulation are a results of the temperature fluctuations. Finally, the change in temperature cannot be explained by the fluctuations in O₃ and is more likely a results from the changes in eddy heat transport.

Utilization of N₂O data from SAMS

The atmospheric lifetime of N₂O is determined by the photochemical removal of the gas in the lower stratosphere. Previous calculations using balloon observations of N₂O as data and/or for validation obtained a lifetime for N₂O of about 150-175 years. Data for N₂O is available from the SAMS instrument on Nimbus-7 covering the region from 50°S to 70°N, 25 km to 50 km where 80% of the removal occurs. Using the observed N₂O data to check against the model calculated distribution, we concluded that calculated lifetimes as short as 114 years are consistent with the data.

Photochemical Studies using LIMS data

We incorporated the observed O₃, H₂O, and temperature from LIMS as input into our diurnal model. In this mode of operation, the values for local temperature, O₃ and H₂O are assigned the observed values and the concentrations for the other long-lived trace gases are taken from previous model simulations. The model is then used to calculate the concentrations of the short-lived species assuming local photochemical equilibrium. The model results are compared with the LIMS observed NO₂ and HNO₃.

Publication in Preparation

Schneider, H-R, M.K.W. Ko, C.A. Peterson and E. Nash, Interannual Variation of Ozone : Interpretation of 4 years of Nimbus 7 SBUV Observations.

Ko, Malcolm, N-D Sze and D. K. Weisenstein, Validation of Atmospheric Lifetimes for Source Gases Using N₂O Data from SAMS.

Studies of the antarctic ozone hole:
Analysis of perturbations to global ozone trends

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Research Objectives

The general objective of this program is to refine our understanding of the chemistry of the antarctic ozone hole, and to study the impact of polar phenomena (heterogeneous chemistry, dilution effect, denitrification) on the global ozone trends. The specific goals are:

- Further studies of the dilution of the antarctic ozone loss using our two-dimensional chemistry transport model; comparison to other model results and observational data.
- Incorporation of heterogeneous processes into our 2-D model, both in the polar regions and in the global atmosphere, in a manner consistent with available laboratory data and field measurements.
- Assessment of the impact of heterogeneous reactions both for the present and future atmosphere; assessment of the future behavior of the antarctic ozone hole and its impact on global ozone trends; assessment of the coupling among ozone and temperature perturbations, circulation changes, and dynamical redistribution.

Progress and Results

Our work during the first year has concentrated on three general areas: a) studies of the photochemistry of the Antarctic stratosphere; b) assessment of the impact of high-latitude chemistry on the HO_x and O_3 budgets; c) impact of high-latitude and global heterogeneous chemistry on ozone trends. The main results of our research are as follows:

- We have assessed the impact of new kinetic data for formation and photolysis of Cl_2O_2 on the partitioning of chlorine species and calculated ozone reductions within the Antarctic polar vortex. Calculations indicate that the observed ClO and ClNO_3 column densities near the edge of the vortex are consistent if we adopt the new kinetic data. Decreases in the observed column densities of HCl and ClNO_3 towards the core of the vortex suggest an increase in ClO with latitude, with a correspondingly larger calculated reductions of ozone. The ozone reductions calculated with the new kinetic data are still consistent with observations, if we consider the spread in both the ozone and ClO measurements and mixing of air within the vortex.
- We have incorporated heterogeneous chemistry in our 2-D model, both on Polar Stratospheric Clouds (PSCs) and on the global sulfate layer.
- Model results indicate that the heterogeneous reaction of ClNO_3 with H_2O (ice, aerosol) could be the primary source of HO_x at high latitudes winter (greater than 60°) if the atmosphere has been

depleted in NO_x but not in HNO_3 , and if the equivalent first-order rate of this reaction is about 10^{-6} s^{-1} . Inclusion of this reaction in our model increased the calculated HO_x abundances by almost a factor of 10, with corresponding changes in the partitioning between HCl and other chlorine species. Ozone loss below 22 km occurred in this case primarily through chlorine and HO_x catalytic cycles.

- We have started the assessment of the impact of heterogeneous chemistry by considering two cases: 1) heterogeneous reactions occurring in a denitrified atmosphere on PSCs at high latitudes during winter; 2) heterogeneous reaction of HCl with ClNO_2 occurring year-round in the global sulfate layer, with a reaction efficiency of about 10^{-3} . Both cases yield calculated ozone trends for the past 20 years consistent with those derived by the NASA Ozone Trends Panel. However, the calculated future ozone trends are dramatically different. Possibility (1) yields ozone reductions in the year 2060 of order 10% relative to 1985 at high latitudes, winter. The assumptions in (2) result in calculated ozone reductions of order 20 - 30% for the same year, season, and latitude. Uncertainties in the kinetic data for heterogeneous reactions indicates the need for further sensitivity studies, and for validation of model results by comparing to data on other trace species (ie., ClO).

Conference Presentations

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze (1989) "Impact of new kinetic data for the chemistry of the Antarctic stratosphere," presented at the Spring Meeting of the American Geophysical Union, Baltimore, MD, May 7-12, 1989. EOS, 70, 299.

Rodriguez, J. M., M. K. W. Ko, N. D. Sze, and D. Weisenstein (1989): "Global implications of heterogeneous chemistry: Assessment utilizing a two-dimensional model," presented at the Fifth Scientific Assembly of the International Association of Meteorology and Atmospheric Physics (IAMAP), Reading, England, July 31-August 11, 1989.

Publications

D. W. Fahey, D. M. Murphy, K. K. Kelly, M. K. W. Ko, M. H. Proffitt, C. S. Eubank, G. V. Ferry, M. Loewenstein and K. R. Chan (1989) "Measurements of nitric oxide and total reactive nitrogen in the Antarctic stratosphere: Observations and chemical implications," J. Geophys. Res., in press.

Publications in preparation

Rodriguez, J. M., M. K. W. Ko and N. D. Sze (1989): "Partitioning of chlorine species inside the Antarctic polar vortex."

Rodriguez, J. M., M. K. W. Ko, N. D. Sze and D. Weisenstein (1989): "Global implications of heterogeneous chemistry."

Research Summary 1988-1989

A. Title of Research Task

Interactions of Atmospheric Chemical, Radiative, and Dynamical Processes: Research Studies with and Further Development of the LLNL Two-Dimensional Global Atmospheric Model

B. Investigators and Institutions

Principal Investigator: Dr. Donald J. Wuebbles

Co-Investigators: Dr. Peter S. Connell
Dr. Keith E. Grant
Dr. Douglas E. Kinnison

C. Research Objectives

The primary goals of this project are the further development of the LLNL two-dimensional chemical-radiative-transport model of the troposphere and stratosphere, and the application of this model to research studies on the middle atmosphere. Model capabilities are being extended towards improving understanding of the key processes that control the distribution of ozone and other important species in the global atmosphere. Research studies are primarily oriented at assessing the past and possible future changes in ozone from natural and human-induced causes, and to improve understanding of observations of global trace constituent distributions.

D. Progress and Results

The two-dimensional model has been applied to a number of research studies during 1988 and 1989. LLNL scientists have also participated in several international assessment efforts in support of NASA during this time period. Past trends in ozone and temperature were analyzed with the model for the Trends Panel Report (we also contributed to the writing of this report being published through NASA and other organizations). For the recent Scientific Assessment of Stratospheric Ozone: 1989 (being published by WMO), we not only provided model calculations for trace gas scenario effects on ozone and an analysis of ozone depletion potentials for CFCs and other compounds, but also coordinated the preparation and writing of one of the four chapters. In 1988, we helped coordinate and participated in an international two-dimensional intercomparison of atmospheric models sponsored by NASA.

Research studies with the two-dimensional model include: an analysis of trends in ozone and temperature over the past thirty years, including a careful evaluation of the possible effects on ozone resulting from atmospheric nuclear testing in the early 1960s; an analysis and sensitivity study of potential effects of high speed commercial aircraft on stratospheric ozone; an analysis of carbon-14 and other tracers produced from nuclear tests to determine their usefulness for validating the treatment of troposphere-stratosphere

exchange processes in the 2-d model; and an analysis of the 11-year solar cycle for its effects on upper stratospheric ozone and temperature.

The two-dimensional model has been continued to be improved and refined. Additional layers have been added to the model to extend it into the lower mesosphere and to improve the resolution in the troposphere. The solar and infrared radiative submodels have extensively revised to provide improved treatment of scattering and cloud-related processes. Determination of upper stratospheric cooling rates has also been improved. At the same time, computational speed has been improved, such that the current model runs as fast as earlier versions.

E. Publications

- Connell, P. S., and D. J. Wuebbles, "Evaluating CFC Alternatives from the Atmospheric Viewpoint," Air and Waste Management Assoc. paper 89-5.7, 1989.
- DeLuisi, J. J., D. U. Longenecker, C. L. Mateer, and D. J. Wuebbles, "An Analysis of Northern Middle-Latitude Umkehr Measurements Corrected for Stratospheric Aerosols for 1979-1986", *J. Geophys. Res.* 94, 9837-9846, 1989.
- Grant, K. E., R. G. Ellingson, and D. J. Wuebbles, "Sensitivity of a Two-Dimensional Chemistry-Transport Model to Changes in Parameterizations of Radiative Processes", in *IRS '88: Current Problems in Atmospheric Radiation*, J. Lenoble and J-F. Geleyn, editors, A. Deepak Publishing, Hampton, Va., 1989.
- Johnston, H., D. E. Kinnison, and D. J. Wuebbles, "Nitrogen Oxides from High Altitude Aircraft: An Update of Potential Effects on Ozone", *J. Geophys. Res.* 94, in press, 1989.
- Kinnison, D. E., H. Johnston and D. Wuebbles, "Ozone Calculations with Large Nitrous Oxide and Chlorine Changes", *J. Geophys. Res.* 93, 14165-14175, 1988.
- Reinsel, G. C., G. C. Tiao, S. K. Ahn, M. Pugh, S. Basu, J. J. DeLuisi, C. L. Mateer, A. J. Miller, P. S. Connell, and D. J. Wuebbles, "An Analysis of the 7-Year Record of SBUV Satellite Ozone Data: Global Profile Features and Trends in Total Ozone", *J. Geophys. Res.* 93, 1689-1703, 1988.
- Wuebbles, D. J., and D. E. Kinnison, "A Two-Dimensional Model Study of Past Trends in Global Ozone", *Proceedings, 1988 Quadrennial Ozone Symposium*, in press, 1989.
- Wuebbles, D. J., K. E. Grant, P. S. Connell, and J. E. Penner, "The Role of Atmospheric Chemistry in Climate Change", *J. Air Pollution Control Assoc.* 39, 22-28, 1989.

A. Two-Dimensional Model Studies of the Middle Atmosphere

- B.** R. R. Garcia, National Center for Atmospheric Research, Boulder, CO
S. Solomon, NOAA / Aeronomy Laboratory, Boulder, CO
J. T. Kiehl, National Center for Atmospheric Research, Boulder, CO

- C.** The two-dimensional model of Garcia and Solomon will be used to study several aspects of radiative-chemical-dynamical coupling in the middle atmosphere. The proposal consists of three components: Improvements and extensions of our present 2D model; studies of radiative/photochemical coupling in the contemporary middle atmosphere; and studies of possible interactions among radiation, dynamics and photochemistry that may be important in the future atmosphere due to changes in CFCs, carbon dioxide, methane, and nitrous oxide.
- D.** The 2D model has been improved by the addition of an IR transfer model developed by J. Kiehl. This model uses a band formulation to explicitly compute IR heating/cooling rates. The model domain had been extended to include the troposphere. Model dynamics have been reformulated to include explicit solution of the zonal mean momentum equation. The new dynamical formulation should allow studies of tropical dynamics not possible with the previous version wherein the zonal wind was assumed to be in thermal wind balance with the temperature field. A single-wavenumber planetary wave model has been coupled to the 2D model to study seasonal and interhemispheric differences in transport due to planetary wave activity.
- E.** Papers on the response of the stratosphere to multiple anthropogenic perturbations (CFCs + CO₂ + CH₄) and on the new model dynamics are in preparation.

NASA RESEARCH SUMMARY

Grant No. NAGW-1605

A. Title of Research Task:

Zonally-Averaged Model of Dynamics, Chemistry and Radiation for the Atmosphere

B. Principle Investigator:

Ka-Kit Tung, Professor of Applied Mathematics, University of Washington

C. Abstract of Research Objectives:

To construct a physically based 2-D model with coupled dynamics, chemistry and radiation; to use such a model to simulate the present date distribution of trace gases in the stratosphere and to assess future change.

D. Summary of Progress and Results:

We have completed the implementation of the diagnostic model using NMC temperature as input from which both the advective and diffusive transports are deduced. We have recently added a narrow-band radiative transfer model, which has an accuracy of better than 10% when compared to the line-by-line calculations. We have also completed the implementation of the chemistry module, with O_x , HO_x , NO_x and ClO_x cycles. The simulation of present date distribution of many species, including ozone, using the coupled model showed great improvements over previous generations of models.

E. Publications:

K.K. Tung and H. Yang: *Dynamical component of seasonal and year-to-year changes in Antarctic and global ozone*. J. of Geophys. Research, 93, 12537-12559, 1988.

K.K. Tung and H. Yang: *Dynamic variability of column ozone*, J. of Geophys. Research, 93, 11123-11128, 1988.

H. Yang, K.K. Tung and E.P. Olaguar: *Two-D model simulation of ozone climatology and year-to-year variations*, in Proceedings of Quadrennial Ozone Symposium, 1988.

H. Yang, K.K. Tung and E.P. Olaguar: *Nongeostrophic theory of zonally averaged circulation. Part II: E-P fluxes and isentropic mixing coefficients*, J. Atmos. Sci., accepted 1989.

Research Summary

Upper Atmosphere Theory and Data Analysis Program

A) Stratosphere Chemistry in a 2-D Model with Residual Circulation.

B) Paul D. Guthrie
Laboratory for Atmospheres
Goddard Space Flight Center

Charles H. Jackman
Laboratory for Atmospheres
Goddard Space Flight Center

C) The objective of this research has been to examine the effects of chemical perturbations on the stratosphere using models which can incorporate fully interactive radiative, chemical and dynamical responses, in the context of a zonally averaged model.

D) Model runs for the unperturbed, chlorine-perturbed and simultaneously chlorine-and CO₂-perturbed cases were completed using the JPL-87 chemical kinetics data. The base case has been analyzed and submitted for publication. A paper analyzing the perturbed cases is in preparation. The perturbed cases show substantial sensitivity of the predicted column ozone depletion to the perturbations affecting lower stratospheric temperature, but less so for dynamical perturbations. The column ozone distribution changed substantially when the kinetics data was changed. This implies a greater-than-expected uncertainty in predicted latitude distributions of ozone depletion, due to uncertainty about the accuracy and completeness of the chemical kinetics data set.

Work under this task has been terminated.

E) "On the sensitivity of a Residual Circulation model to differences in input temperature data," P. D. Guthrie, C. H. Jackman, T. L. Kucsera and J. E. Rosenfield, J. Geophys. Res., in press, 1989.

"The sensitivity of total ozone and ozone perturbation scenarios in a two-dimensional model due to dynamical inputs," C. H. Jackman, A. R. Douglass, P. D. Guthrie, and R. S. Stolarski, J. Geophys. Res., 94, 9873-9887, 1989.

"On the latitude dependence of ozone depletion predictions," P. D. Guthrie, T. L. Kucsera and C. H. Jackman, "Proceedings of the Quadrennial Ozone Symposium, Gottingen," in press, 1989.

"A prognostic 2-D model with coupled chemistry, radiation and transport I: the base case," P. D. Guthrie, T. L. Kucsera, C. H. Jackman and J. E. Rosenfield, submitted to J. Geophys. Res., 1989.

A. Fast Two-dimensional Model

B. Principal Investigator:

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Co-Investigators:

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R. S. Stolarski
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Greenbelt, MD 20771

C. Research Objectives

The objective of this research is to use a two-dimensional (altitude and latitude) model of the atmosphere to investigate problems relating to the variability of the dynamics and temperature of the atmosphere on the ozone distribution, solar cycle variations of atmospheric constituents, the sensitivity of model results to tropospheric trace gas sources, and assessment computations of changes in ozone related to manmade influences.

D. Progress and Results

We have contrasted two-dimensional (2D) model results in which the odd nitrogen family was transported together with model results in which the odd nitrogen species were transported separately and found that family approximations are adequate for perturbation scenario calculations. However, because HNO_3 data are available for comparison with calculated values and family approximations are poor for HNO_3 during winter, in future model simulations HNO_3 will be transported separately.

The sensitivity of ozone and ozone perturbation scenarios due to dynamical inputs were investigated and it was found that although total ozone was extremely sensitive to the circulation between 1000 and 100 mbar, the perturbation scenarios were relatively insensitive to the dynamical inputs.

The effect of solar proton events (SPEs) on the middle atmosphere during the two solar cycle period from 1963-85 was investigated and it was found that: 1) odd nitrogen does not build up over solar cycle periods but decreases to ambient values in 2-6 months following even a major SPE and 2) only the August 1972 SPE caused significant stratospheric ozone depletion at high latitudes.

All eight assessment scenarios of interest were investigated for the United Nations Environmental Program "Scientific Assessment of Stratospheric Ozone:1989" with the use of our 2D model.

We took part in an international 2D model intercomparison held at Virginia Beach, VA in September 1988 and have been actively involved in the conference proceedings which will be published in August 1989 concerning that meeting.

We cooperate with the three-dimensional (3D) modeling effort at NASA/GSFC (Code 616) and provide initial conditions from our 2D model for use in the 3D model.

E. Journal Publications

Douglass, A. R., C. H. Jackman, and R. S. Stolarski, Comparison of model results transporting the odd nitrogen family with results transporting separate odd nitrogen species, J. Geophys. Res., 94, 9862-9872, 1989.

Jackman, C. H., A. R. Douglass, P. D. Guthrie, and R. S. Stolarski, The sensitivity of total ozone and ozone perturbation scenarios in a two-dimensional model due to dynamical inputs, J. Geophys. Res., 94, 9873-9887, 1989.

Jackman, C. H., A. R. Douglass, and P. E. Meade, The effects of solar particle events on the middle atmosphere, in press, Middle Atmosphere Handbook, 1989.

Jackman, C. H., A. R. Douglass, P. A. Newman, and P. D. Guthrie, Effect of computed horizontal diffusion coefficients on two-dimensional assessment studies, in press, Proceedings of the Quadrennial Ozone Symposium held at Gottingen, West Germany, August 8-13, 1988.

Douglass, A. R., C. H. Jackman, and R. S. Stolarski, Two-dimensional model comparisons of odd nitrogen family chemistry with separate calculations for the odd nitrogen species, in press, Proceedings of the Quadrennial Ozone Symposium held at Gottingen, West Germany, August 8-13, 1988.

UATDAP Research Summary 1988-1989

A. Title of Research Task

Modeling of Chemistry and Transport in a Two-Dimensional Model of the Terrestrial Stratosphere and Mesosphere

B. Investigations and Institutions

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C. Abstract of Research Objectives

The focus of our research program is the achievement of a quantitative understanding of the spatial distribution and temporal variation of chemical species in the terrestrial middle atmosphere, with emphasis on ozone. Although not directed at assessments of anthropogenic impacts, our activities contribute to a refinement of model descriptions of chemical and dynamical processes that are needed for assessment tasks.

D. Summary of Progress and Results

1. One week (May 1-7, 1979) of data from the Nimbus 7 Limb Infrared Monitor of the Stratosphere (LIMS) was analyzed in detail, with emphasis on the ozone abundance and its temperature sensitivity between 0.1 and 6 mbar, covering the upper stratosphere and lower mesosphere. The zonally averaged ozone profile (30°-35°N latitude) is compared with results from a simplified photochemical model that assumes ozone to be in photochemical steady state. The model ozone profile is systematically lower than the observed profile. Changes in O₂ photolysis and O₃ formation could eliminate most of the differences in the whole altitude range. Thus one does not have to invoke one or more missing key reactions in current photochemical models in order to explain this systematic discrepancy. The LIMS-derived values for the sensitivity of ozone to changes in temperature, θ_L , are compared with equilibrium model calculations, θ_E , which include the temperature-driven opacity feedback effect on photodissociation rate constants. Given the noise of the data, there is fair agreement in the mesosphere, but below 1 mbar, θ_L/θ_E decreases with increasing pressure. In the upper stratosphere the LIMS-derived θ values can be explained by a combination/superposition of waves with 1- to 5-day periods.
2. We examined the consequences of the eruption of the El Chichon volcano on the Earth's stratospheric chemistry. Formed after the eruption, the volcanic aerosol cloud, with a peak particle density at 27 km, was very efficient at altering the radiation field. A combination of this radiation change and the effect of a temperature variation of a few degrees causes the abundance of O₃ to decrease by 7% at 24 km, in good agreement with the SBUV measurements of a 5-10% decrease. A heterogeneous

reaction catalyzed by aerosol surfaces which transforms ClNO_3 into HCl provides a pathway for sequestering NO_x , and at the same time reduces ClNO_3 in favor of HCl . The inclusion of this reaction in the model leads to a satisfactory single-step explanation of the otherwise puzzling observations of significant decreases in NO and NO_2 and increases in HCl .

3. The gas-phase recombination of chlorine monoxide (ClO) has been investigated under the conditions of pressure and temperature that prevail in the Antarctic stratosphere during the period of maximum ozone (O_3) disappearance. Measured rate constants are less than one-half as great as the previously accepted values. One-dimensional model calculations based upon the new rate data indicate that currently accepted chemical mechanisms can quantitatively account for the observed O_3 losses in late spring 17 September to 7 October.
4. Extensive testing of the advective scheme, proposed by Prather (1986), has been carried out in support of the Caltech-JPL two-dimensional model of the middle atmosphere. Five types of numerical experiments including simple clock rotation and pure advection in 2-D have been investigated in detail. Upon comparing our numerical model results with analytic solutions, we find that the new algorithm can faithfully preserve concentration profiles and has essentially no numerical diffusion.
5. Using the Caltech-JPL two-dimensional transport model, with transport coefficients taken from Yang and Tung (1989), we have studied the time evolution of excess carbon 14 in the stratosphere and the troposphere from October, 1963 to December, 1966. The model provides a satisfactory simulation of the observed data. Due to the impulsive nature of its source, initial distributions of excess carbon 14 exhibit large spatial gradients. This permits important constraints on the range of diffusive transport coefficients in the lower stratosphere to be derived.

E. Journal Publications

- Froidevaux, L., Allen, M., Berman, S., and Daughton, A. (1989). The mean ozone profile and its temperature sensitivity in the upper stratosphere and lower mesosphere: An analysis of LIMS observations. *J. Geophys. Res.* **94**, 6389-6417.
- Michelangeli, D.V., Allen, M., and Yung, Y.L. (1989). El Chichon volcanic aerosols: Impact of radiative, thermal and chemical perturbations. *J. Geophys. Res.*, in press.
- Shia, R.-L., Yung, Y.L., Allen, M., Zurek, R.W., and Crisp, D. (1989). Sensitivity study of advection and diffusion coefficients in a two-dimensional stratospheric model using excess carbon 14 data. *J. Geophys. Res.*, in press.
- Sander, S.P., Friedl, R.R., and Yung, Y.L. (1989). ClO dimer in polar stratospheric chemistry: Rate of formation and implications for ozone loss. *Science*, in press.
- Shia, R.-L., Ha, Y.L., Wen, J.-S., and Yung, Y.L. (1989). Two-dimensional atmospheric transport and chemistry model: Numerical experiments with a new advection algorithm. *J. Geophys. Res.*, in press.

Biennial Research Summary

STRATOSPHERIC RADIATIVE PROCESSES AND THE 2-D CHEMICAL TRACER TRANSPORT CIRCULATION

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ABSTRACT

The distribution of O₃ and other trace gases is most strongly influenced by meridional transport at levels in the middle and lower stratosphere. GCM experiments show that the transport at these levels can be approximated by the diabatic circulation, which can be derived diagnostically from the net radiative heating rates. I am developing a hierarchy of fast, accurate methods for finding stratospheric net radiative heating rates. These heating rates will be used to specify the transport circulation in the Caltech 2-D Chemical Tracer Transport Model.

SUMMARY OF PROGRESS AND RESULTS

2-dimensional chemical tracer transport models are the best existing tools for studying the response of the stratosphere to observed changes in thermal structure and composition. The advective component of the meridional transport in these models is approximated by the diabatic circulation, which can be derived diagnostically from the net radiative heating rates. Accurate radiative transfer models are essential for this application because the net radiative heating rates are obtained by subtracting the almost-equal solar heating rates and thermal cooling rates at each stratospheric level. Small errors in the solar or thermal components can produce enormous errors in net heating rates and the strength of the derived diabatic circulation. This is particularly true at levels in the middle and lower stratosphere, where these components usually differ by less than 20%. I recently conducted an intercomparison of thermal cooling algorithms used by several 2-d groups, and found cooling rate errors twice this large. This result has serious implications for the validity of the 2-d modeling results derived by these groups. Our Quasi-Random Model rarely produces cooling rate errors larger than 5%, but requires much more computer time than those used by other groups. Faster radiative transfer algorithms are essential in 2-d chemical tracer transport models, because net radiative heating rates must be recomputed often as the atmospheric temperature and composition changes.

The Caltech radiative transfer model accounts for all important radiative processes at levels between the surface and 65 km. A Voigt Quasi-Random model is used to find the absorption by gases, and a delta-Eddington/Adding method is used to find fluxes and heating rates in absorbing, scattering atmospheres. This model agrees well with an accurate line-by-line model, but it requires much more computing time than the simpler models used by other 2-D modeling groups. We propose to address these problems by developing and implementing a new class of Correlated-k model. This model should provide the speed and accuracy needed in a broad range of stratospheric tracer transport modeling applications.

**Upper Atmosphere Theory and Data Analysis
(UATDAP) Program
1988-1989 Research Summary**

A. Title of Research Task

MESOSPHERIC THEORY

B. Investigators and Institutions

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Collaborators

Y. Yung (Caltech), M. Allen and D. Crisp (JPL and Caltech)

(See the UATDAP Research Summary by Y. Yung et al., "Modeling of Chemistry and Transport with a Two-Dimensional Model of the Terrestrial Stratosphere and Mesosphere".)

C. Abstract of Research Objectives

This research task supports a collaborative effort between investigators at Caltech and JPL to understand quantitatively the structure and circulation of the upper atmosphere and the distribution there of photochemically or radiatively important trace constituents. This is done through numerical simulations of the observed tracer distributions, using one and two-dimensional models of coupled photochemical, dynamical and radiative processes.

D. Summary of Progress and Results

Extensive testing of the advective transport scheme proposed by Prather (1986) has been carried out in support of the Caltech-JPL two-dimensional model of the middle atmosphere. The implemented

algorithm faithfully preserves concentration profiles and has essentially no numerical diffusion.

The Caltech-JPL two-dimensional transport model, with advective zonal-mean winds and eddy mixing coefficients taken from Yang and Tung (1989), has been used to simulate the time evolution of excess ^{14}C in the stratosphere and troposphere during 1963-1966. Due to the impulsive nature of its source, initial distributions of excess ^{14}C exhibit large spatial gradients. This permits important constraints to be derived on the range of the "effective" diffusive mixing in the lower stratosphere.

E. Journal Publications

Shia, R.-L., Y. L. Yung, M. Allen, R. W. Zurek and D. Crisp (1989). Sensitivity study of advection and diffusion coefficients in a two-dimensional stratospheric model using excess carbon 14 data. J. Geophys. Res., in press.

BIENNIAL RESEARCH SUMMARY

A. Dynamical Investigations of the Middle Atmosphere with a 2-D Model

B. Dr. Matthew H. Hitchman, Principal Investigator
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Dr. Guy Brasseur, Co-Investigator
National Center for Atmospheric Research

C. The fundamental goal is to improve our understanding of dynamics and tracer transport in the middle atmosphere through the use of a two dimensional numerical model. The model contains approximately 50 trace species, a detailed radiative code, and has fully interactive zonal mean and wave dynamics, including a new method of closure for the effects of planetary scale Rossby waves. Five areas of study are emphasized for the three year period 1 September 1988 - 31 August 1991: 1) a complete exploration of the impact of this new Rossby wave parameterization on the meridional circulation and tracer distributions, 2) transport at low latitudes, including the roles of photochemistry and wave driving in the semiannual and quasibiennial oscillations, 3) modeling the effects of heterogeneous processes on the ozone layer, and 4) systematically assessing the relative roles of annual insulation variation and wave driving by gravity, Rossby, and Kelvin waves in establishing the observed basic state.

D. Our grant began in September of 1988. 1) The main emphasis since that time has been in exploring the Rossby wave parameterization. We have performed many sensitivity studies and have diagnosed the feedbacks that result. In conjunction with Dr. Walter Robinson of the University of Illinois at Champaign-Urbana, we are comparing the WKBJ group velocity representation of Rossby wave activity propagation and absorption with a steady state linear wave model. There is general agreement and, where there are differences, the reasons are clear. 2) We have modified how winds are calculated in the model such that tropical winds have the capability to interact with gravity and Kelvin waves. We have recently added Kelvin waves to the model using the method of Plumb (1977). Initial results include a reasonable semiannual oscillation. 3) The model now has a threshold temperature below which polar stratospheric clouds are assumed to form and create additional odd chlorine. The parameterization has been tuned to yield spring ozone losses similar to what has been recently observed. Large uncertainties in the rates of microphysical processes limit the utility of this parameterization. 4) We have begun the fundamental study of causes of the basic state by calculating radiative equilibrium temperatures and exploring the differences that result from different basic assumptions regarding boundary conditions and allowed flows.

We have performed many model runs of perturbed trace gas scenarios in conjunction with the model intercomparison workshop held in Virginia Beach during September of 1988, and for the document "Scientific Assessment of Stratospheric Ozone: 1989", and have contributed sections and a summary of Chapter 3 for that document. The first publication below reflects work on understanding recent global ozone changes. The second describes the Rossby wave parameterization. The third documents our 2-D model in greater detail. In the fourth publication, the 2-D model was crucial in understanding the mechanism of how gravity wave driving causes the separated polar winter stratopause.

E. Publications

- 1) Brasseur, G., M. H. Hitchman, P. C. Simon, and A. De Rudder, 1988: Ozone reduction in the 1980's: A model simulation of anthropogenic and solar perturbations. *Geophys. Res. Lett.*, **15**, 1361-1364.
- 2) Hitchman, M. H. and G. Brasseur, 1988: Rossby wave activity in a two-dimensional model: Closure for wave driving and meridional eddy diffusivity. *J. Geophys. Res.*, **93**, 9405-9417.
- 3) Brasseur, G., M. H. Hitchman, S. Walters, M. Dymek, E. Falise, and M. Pirre, 1989: An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere. *J. Geophys. Res.*, in press.
- 4) Hitchman, M. H., J. C. Gille, C. D. Rodgers, and G. Brasseur, 1989: The separated polar winter stratopause: A gravity wave driven climatological feature. *J. Atmos. Sci.*, **46**, 410-422.

A. Title of Research Task

N92-14535 J

Stratospheric Dynamics and Transport Studies

B. Investigators and Institutions

P.I.: Dr. William L. Grose, NASA Langley Research Center
Co-I's: Dr. R. E. Turner, NASA Langley Research Center
Dr. W. T. Blackshear, NASA Langley Research Center
Dr. R. S. Eckman, NASA Langley Research Center

C. Abstract of Research Objectives

A 3-D GCM/transport model will be used to simulate stratospheric circulation and constituent distributions. Model simulations will be analyzed to interpret radiative, chemical, and dynamical processes and their mutual interactions. Concurrent complementary studies will be conducted using both global satellite data and other appropriate data. Comparisons of model simulations and data analysis studies will be used to aid in understanding stratospheric dynamics and transport processes and to assess the validity of current theory and models.

D. Summary of Progress

(1) Revised chemistry formulation implemented in transport model to incorporate explicit transport of O_x , NO_y , Cl_x , HNO_3 , H_2O_s , and H_2O_2 . Conducted 2-year simulation and analysis of seasonal evolution of odd nitrogen and total ozone column and begun comparison with available data. (2) Conducted 2-year simulation of N_2O distribution and begun comparison with SAMS data. Preparing to incorporate explicit transport of N_2O with other families and species in transport model. (3) Conducted multi-year simulation to study dilution effect after formation of Antarctic ozone hole and subsequent breakup of the vortex. (4) Analyzed annual cycle from model simulation to elucidate large-scale transport of ozone between troposphere and stratosphere. (5) Analyzed polar jet instability in Southern Hemisphere using LIMS and SSU data. (6) Performed comparative analysis of stratospheric warmings from multi-year SSU data set.

E. Publications

Grose, W. L., R. S. Eckman, R. E. Turner, and W. T. Blackshear: Global Modeling of Ozone and Trace Gases, in Atmos. Ozone and Its Policy Implications, T. Schneider (Ed.), Elsevier Publ., Amsterdam, 1989.

Miles, T. and W. L. Grose: Upper Stratosphere Polar Jet Instability in the Southern Hemisphere, Geophys. Res. Lett., **16**, 1989.

Grose, W. L., T. Miles, K. Labitzke, and E. Pantzke: Comparison of LIMS Temperatures and Geostrophic Winds with Berlin Radiosonde Temperature and Wind Measurements, J. Geophys. Res., **93**, 1988.

Miles, T. and W. L. Grose: Comparison of Geostrophic and Nonlinear Balanced Winds from LIMS Data and Implications for Derived Dynamical Quantities, PAGEOPH, **129**, 1989.

Grose, W. L. and A. O'Neill: Comparison of Data and Derived Quantities for the Middle Atmosphere of the Southern Hemisphere, PAGEOPH, **129**, 1989.

*Research Summaries FY 1988-89: Upper Atmosphere Theory & Data Analysis Program***A. Stratospheric Chemistry and Transport**

**B. Dr. Michael Prather (P.I.), NASA/GISS
Dr. María M. García (Co-I.), Columbia U.**

C. Research Objectives of this project were to implement chemistry in the 3-D general circulation model of the middle atmosphere developed by Dr. David Rind (GISS) under another task. The objectives were to develop an operational chemical tracer model (CTM) that used the wind fields from the GCM. The first work under this project was to use chemical tracers with simple, first-order losses such as N_2O and then to develop a successively more complex ozone chemistry. A major direction of the CTM is the examination of climate perturbations (predicted by the GCM for doubled CO_2) and their impact on stratospheric circulation and ozone.

D. Progress and Results

A study of the Antarctic ozone hole has been made with a 3-D chemical transport model (CTM) using a linearized photochemistry for ozone. The tracer model uses the winds and convection from the GISS general circulation model ($8^\circ \times 10^\circ \times 23$ layers). The GCM develops an Antarctic circumpolar vortex in early winter with strong westerlies that reverse in Austral spring and the circulation compares favorably with the observed climatologies. A 4-year control run of the CTM with annually repeating winds produces ozone distributions that compare reasonably with the observed climatology. We examine different linearizations of the ozone chemistry and show that the calculated column ozone is sensitive to the chemical time constants in the lower stratosphere. In separate numerical experiments, a hypothetical Antarctic ozone "hole" is induced on September 1 and on October 1; the CTM is integrated for 1 year with a linearized model that assumes standard photochemistry, not including the heterogeneous reactions and unusual chemistry associated with formation of the ozone hole. The initial depletion, assumed to be 90% of the O_3 poleward of $70^\circ S$ between 22 and 200 mbar, amounts to about 5% of the total O_3 in the Southern Hemisphere.

As the Antarctic vortex breaks down and the ozone hole is dispersed, significant depletions to column ozone, of order 10 Dobson units ($\approx 3\%$) occur as far north as $40^\circ S$ during Austral summer. One year later, only 30 % of the original depletion remains, mostly below 100 mbar and poleward of $30^\circ S$. The October 1 initialization is continued for a second year, the ozone hole being reinduced one year later with the same parameterization. The cumulative effects from the year before are noticeable, but add only 20 % to the depletion. A budget analysis for the southern high-latitude stratosphere (10-350 mbar \times $31-90^\circ S$) indicates the ozone hole is replenished equally by photochemical regeneration and by reduced transport of ozone into the troposphere, with a lesser fraction being filled in by an increased flux from the tropical stratosphere.

A model for the chemical mixing of stratospheric air over spatial scales from tens of kilometers to meters was developed (Prather and Jaffe, 1989). Photochemistry, molecular diffusion, and strain (the stretching of air parcels due to wind shear) are combined into a single one-dimensional model. The model is applied to the case in which chemically perturbed air parcels from the Antarctic stratosphere are transported to midlatitudes and strained into thin ribbon-like filaments until they are diffusively mixed with the ambient stratosphere. We find that the parcels may be treated as evolving in chemical isolation until the final mixing. When parcels reach a transverse thickness of 50-100 m in the lower stratosphere, they are rapidly dispersed by the combination of molecular diffusion and strain. The rapidity of the final mixing implies a lower limit to the vertical scales of inhomogeneities observed in the lower stratosphere.

For this sensitivity study, we consider four types of Antarctic air: a control case representing unprocessed polar air; heterogeneous processing by PSCs that has repartitioned the Cl_x and NO_y families; processing that also includes denitrification and dehydration; and all processing plus 90 % ozone depletion. Large abundances of ClO , resulting initially from heterogeneous processing of stratospheric air on PSCs, are sustained by extensive denitrification. (One exception is the case of Antarctic air with major ozone depletion in which ClO is converted rapidly to HCl upon release of small amounts of NO_x as a result of the extremely non-linear Cl_x - NO_y chemical system.) ClO concentrations in the midlatitude stratosphere should be enhanced by as much as a factor of 5 due to the mixing of air processed around the Antarctic vortex and will remain elevated for most of the following season.

Chemical propagation of the Antarctic ozone hole occurs in two phases: rapid loss of ozone in the heterogeneously processed parcels as they evolve in isolation; and more slowly, a relative recovery of ozone over the following months. Another important effect is the transport of denitrified Antarctic air reducing NO_x and hence the total catalytic destruction of ozone throughout the southern midlatitudes. In Antarctic air that has already been depleted of ozone within the vortex, little additional loss occurs during transport, and the propagation of chemically perturbed air acts partially to offset the deficit at midlatitudes caused by dynamical dilution of the ozone hole. In air which has not experienced substantial ozone loss, chemical propagation can generate a net ozone deficit of order 2-3 % at midlatitudes, which may be part of the recently detected trend at northern midlatitudes in late winter.

E. Publications:

Michael J. Prather and José M. Rodriguez. Antarctic Ozone: Meteoric Control of HNO_3 , *Geophys. Res. Lett.*, 15, 1-4, (1988).

Michael J. Prather. European Sources of Halocarbons and Nitrous Oxide: Update 1986, *J. Atmos. Chem.*, 6, 375-406, (1988).

Michael J. Prather, ed. An Assessment Model for Atmospheric Composition, NASA Conference Publication, CP-3203, 64 pp, (1989).

Michael Prather, María M. García, Robert Suozzo, David Rind. Global Impact of the Antarctic Ozone Hole: Dynamical Dilution with a 3-D Chemical Transport Model, *J. Geophys. Res.*, 94, xxxx-xxxx, (1989).

Michael J. Prather and Andrew H. Jaffe. Global Impact of the Antarctic Ozone Hole: Chemical Propagation, *J. Geophys. Res.*, 94, xxxx-xxxx, (1989).

[3-D model results in:] Jackman, C.H., R.K. Seals Jr. and M.J. Prather, eds. 2-D Intercomparison of Stratospheric Models, NASA Conference Publication, CP-3042, 608 pp, (1989).

General Circulation Modeling of Stratospheric Dynamics and Transport

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Research Objectives

The purpose of the research funded under this proposal is to develop and use three dimensional models of stratospheric dynamics and transport together with simplified chemistry to further our understanding of the stratosphere. The dynamical model will be tested at several resolutions with simplified forcing in order to determine the resolution required for transport experiments. The generation of equatorial waves in the model will be studied for varying vertical resolution and tropospheric physical parameterizations in order to determine the feasibility of simulating the quasi-biennial oscillation (QBO). The research on transport will begin with the advection of small number of species (two or three) with parameterized chemistry.

Summary of Progress

During the five months that this proposal has been funded, several of the proposed projects have been initiated. The implementation of a diurnal cycle has been completed and a study of tides in the troposphere and stratosphere is in progress. The radiation parameterization has been further refined to include the effects of Voigt line shapes and the (apparently significant) effects on the stratospheric circulation are being studied.

Short (150 day) simulations at three vertical resolutions (with level spacings of about 3km, 1.5km and 700m) have been performed to examine the effect of vertical resolution on the generation, propagation and absorption of the short vertical wave length, equatorially trapped mixed Rossby gravity waves believed to be important in forcing the QBO. Early analysis indicates that a doubling of the vertical resolution over that typically used may be sufficient to represent these waves adequately, which may make an attempt to simulate the QBO feasible in the near future.

Stratospheric Dynamics

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Research Objectives

A global circulation model is being used to study the dynamical behavior of stratospheric planetary waves (waves having horizontal wavelengths of tens of thousands of kilometers) forced by growing cyclonic disturbances of intermediate scale, typically with wavelengths of a few thousand kilometers, which occur in the troposphere. Planetary scale waves are the dominant waves in the stratosphere, and are important for understanding the distribution of atmospheric trace constituents. Planetary wave forcing by intermediate scale tropospheric cyclonic disturbances is important for producing eastward travelling planetary waves of the sort which are prominent in the southern hemisphere during winter. The same global circulation model is also being used to simulate and understand the rate of dispersion and possible stratospheric climatic feedbacks of the El Chichon volcanic aerosol cloud. By comparing the results of the model calculations with an established data set now in existence for the volcanic cloud spatial and temporal distribution, stratospheric transport processes will be better understood, and the extent to which the cloud modified stratospheric wind and temperature fields can be assessed.

Summary of Progress and Results

A study has been completed, in which average wintertime conditions in the southern hemisphere have been used to study the interactions of cyclone disturbances and planetary scale waves. The results of this study indicate that the dynamics of eastward travelling planetary waves, which dominate the wave spectrum of the wintertime southern hemisphere stratosphere, cannot be properly understood without considering interactions of cyclone disturbances in the troposphere. In the model calculations, only cyclone forcing of planetary waves is allowed, but the general characteristics of the observed planetary wave features are produced: eastward progression with a speed of about 20 degrees of longitude per day, maximum amplitude occurring near 60° south latitude in the upper stratosphere, propagation time from troposphere to stratosphere of 1-3 days, depending on wavelength, and existence of intermitant periods of wave growth and decay. Computed maximum amplitudes of planetary waves are comparable to peak amplitudes observed for

eastward traveling waves in southern hemisphere winter. The lack of coherence observed for planetary waves 1 and 2 between troposphere and stratosphere appears to be due, based on the computations, to nonlinear effects in the stratosphere. Zonal accelerations induced by the planetary wave momentum and heat transports are in the same qualitative sense as observed, such that the stratospheric jet tends to move downwards and polewards with time. There was no irreversible mixing across or outside the polar vortex by the computed waves.

The characteristics of transport processes in the lower stratosphere were illustrated by the behavior of the El Chichon volcanic cloud which was injected into the stratosphere in April of 1982. Because an extensive data set exists concerning cloud properties as functions of space and time, the El Chichon volcanic cloud represents a unique opportunity to study stratospheric transport processes and the climatic feedbacks of the cloud on the stratosphere. We are using a global circulation model coupled with an aerosol microphysical and transport model to compute the behavior of the volcanic cloud as a function of time and position. We have begun initial simulations treating the cloud as a passive tracer. All NMC data required to force the model at the lower boundary 300 mb pressure level have been acquired, spectrally analyzed, and incorporated into a forcing function which represents the coupling with the troposphere as a function of time. Numerical difficulties encountered with this procedure have been resolved, and stratospheric simulations are underway for the years immediately following the El Chichon eruption.

Journal Publications

Young, R. E., and H. Houben, 1989: Dynamics of Planetary-Scale Baroclinic Waves during Southern Hemisphere Winter. *Journal of the Atmospheric Sciences*, **46**, 1365-1383.

N92-14538

A. Stratospheric General Circulation with Chemistry Model (SGCCM)
(RTOP # 673-64-01-20)

B. Principal Investigator: Richard B. Rood
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C. The goal of this project is to enhance our understanding of the fully interactive general circulation of the stratosphere. The strategy of investigation is to construct and analyze models of the system and compare with observations. Parallel studies of observations and model simulations provide the most effective mechanism for understanding stratospheric processes.

D. In the past two years constituent transport and chemistry experiments have been performed using both simple single constituent models and more complex reservoir species models. Winds for these experiments have been taken from our data assimilation effort (Stratospheric Data Analysis System (STRATAN), RTOP # 673-41-43-20). The application of winds from data assimilation to chemistry and transport studies is unique of this research effort.

Winds from STRATAN allow the quantitative computation of stratospheric transport. This has been verified by comparison of modeled ozone behavior to ozone behavior observed by the Limb Infrared Monitor of the Stratosphere (LIMS). By using winds from STRATAN meaningful transport experiments can be carried out at much lower resolution than if a free running general circulation model (GCM) was used. Because of the great cost of chemical models, the ability to run at coarse resolutions is particularly important.

In an application of the three-dimensional (3D) model to stratospheric chemistry problems, the behavior of nitric acid in the lower stratosphere has been studied. By studying the manner in which the modeled nitric acid diverges from the LIMS observations, it has been possible to offer additional information on the longstanding problem of wintertime nitric acid chemistry. These results indicate the need for a low light source. The results strongly depend on the use of a 3D model, and comparison to 3D data.

Collaboration with the 2D modeling effort at Goddard (C. Jackman, PI) has been increased. This collaboration is exemplified by the use of the 2D model to generate production and losses for the single constituent models, the development of algorithms to generate 3D initial conditions from the 2D model, and the use of the 3D model to guide improvement of the 2D model parameterizations.

Modeling changes: The grid point GCM has been dropped. A version of the Community Climate Model is operational (spectral GCM). The radiation model has been improved, and its computational speed has been reduced 70%. Numerous simple single constituent models have been developed. A twelve reservoir species model has been developed.

E. The publication list showing the most recent publications for the Stratospheric General Circulation with Chemistry Project is attached. Numerous papers are in preparation.

SGCCP PUBLICATIONS (as of 9/13/89)

Published Papers

32. Rood, R. B., D. J. Allen, W. E. Baker, D. J. Lamich, and J. A. Kaye, "The use of assimilated stratospheric data in constituent transport calculations," J. Atmos. Sci., 46, 687-701, 1989.
38. Wu, M. F., M. A. Geller, E. R. Nash, and M. E. Gelman, "Global atmospheric circulation statistics--four year averages," NASA Technical Memorandum 100690, June 1987.
41. Geller, M. A., and M.-F. Wu, "Troposphere-stratosphere general circulation statistics," Transport Processes in the Middle Atmosphere, (G. Visconti and R. Garcia, eds.), D. Reidel Publishing Co., 3-17, 1987.
42. Chao, W. C., "On the origin of the tropical intraseasonal oscillation," J. Atmos. Sci., 44, 1940-1949, 1987.
43. Kaye, J. A., and R. B. Rood, "Chemistry and transport in a three-dimensional stratospheric model chlorine species during a simulated stratospheric warming," J. Geophys. Res., 94, 1057-1083, 1989.
44. Rosenfield, J. E., M. R. Schoeberl, and P. A. Newman, "Antarctic spring-time ozone depletion computed from temperature observations," J. Geophys. Res., 93, 3833-3849, 1988.
45. Kaye, J. A., "Mechanisms and observations for isotope fractionation of molecular species in planetary atmospheres," Rev. Geophys., 25, 1609-1658 1987.
46. Geller, M. A., M.-F. Wu, and E. R. Nash, "Satellite data analysis of ozone differences in the Northern and Southern Hemispheres," Pure & Appl. Geophys., 130, 263-275, 1989.

47. Geller, M. A., "Solar cycles and the atmosphere," Nature, 332, 584-585, 1988.
48. Kaye, J. A., R. B. Rood, and D. J. Allen, "Variability of chlorine containing species as revealed by three-dimensional stratospheric transport and chemistry models," Proceedings of Quadrennial Ozone Symposium, August 8-13, 1988, Gottingen, FRG.
49. Rood, R. B., and J. A. Kaye, "Stratospheric ozone models and super-computers," Proceedings of the Fourth International Conference on Supercomputing, April 30-May 5, 1989, Santa Clara, California.
50. Rosenfield, J. E., "A simple parameterization of ozone infrared absorption for atmospheric heating rate calculations," J. Geophys. Res., (submitted), 1989.
51. Rood, R. B. J. A. Kaye, D. J. Allen, W. E. Baker, and D. J. Lamich, "The use of winds and temperatures from a stratospheric assimilation model in three-dimensional constituent transport studies," Proceedings of Quadrennial Ozone Symposium, August 8-13, 1988, Gottingen, FRG.
52. Rood, R. B., J. A. Kaye, A. R. Douglass, D. J. Allen, S. Steenrod, and E. M. Larson, "Wintertime nitric acid chemistry: Implications from three-dimensional model calculations," J. Atmos. Sci., (submitted), 1989
53. Kaye, J. A. and R. B. Rood, "Simulations of Short-Term Variability of Stratospheric Trace Constituents," Proceedings of the 28th International Astrophysical Colloquium, "Our Changing Atmosphere," Leige, Belgium, June 1989.
54. Kaye, J. A., R. B. Rood, D. J. Allen, E. M. Larson, and C. H. Jackman, "Three Dimensional Simulation of Spatial and Temporal Variability of Stratospheric Hydrogen Chloride," Geophys. Res. Lett., (accepted), 1989.

N92-14539 J

A. Stratospheric Data Analysis System (STRATAN)
(673-41-43-20)

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B. The goal of this project is to produce state-of-the-art stratospheric analyses using a coupled stratosphere-troposphere data assimilation system (STRATAN). These analyses can be applied to stratospheric studies of all types. Of importance to this effort is the application of STRATAN to constituent transport and chemistry problems (Stratospheric General Circulation with Chemistry Model (SGCCM), RTOP # 673-64-01-20)

C. During the past two years, 3 months of assimilation have been completed from the 1978-1979 Limb Infrared Monitor of the Stratosphere (LIMS) period. Assimilation for January and February 1989 have been completed. The 1989 experiments were in support of an Airborne Arctic Stratosphere Expedition theory proposal (R. Stolarski, PI). Both of these assimilation experiments are continuing.

STRATAN analyses have been compared to NMC (National Meteorology Center) analyses and to atmospheric profile data. These comparisons indicate that STRATAN does indeed produce a state-of-the-art analysis. These comparisons have also indicated several problem areas that compel improvements to the assimilation system.

The most important product of STRATAN is the wind analysis. The winds from STRATAN are very different from geostrophic winds from the NMC analyses and compare much better to direct wind measurements. Transport calculations confirm that winds from STRATAN are indeed a better measure of stratospheric winds.

The quality of the winds from STRATAN demonstrate the use of assimilation techniques in stratospheric analysis. We plan to initiate constituent assimilations in the next proposal cycle. Assimilation of data into comprehensive dynamical and photochemical models provide s a mechanism for taking full advantage of all the space and time information that is contained in satellite and ground based measurements.

E. The publication list showing the most recent publications for the Stratospheric General Circulation with Chemistry Project is attached. Numerous papers are in preparation.

SGCCP PUBLICATIONS (as of 9/13/89)

Published Papers

32. Rood, R. B., D. J. Allen, W. E. Baker, D. J. Lamich, and J. A. Kaye, "The use of assimilated stratospheric data in constituent transport calculations," J. Atmos. Sci., 46, 687-701, 1989.
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42. Chao, W. C., "On the origin of the tropical intraseasonal oscillation," J. Atmos. Sci., 44, 1940-1949, 1987.
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53. Kaye, J. A. and R. B. Rood, "Simulations of Short-Term Variability of Stratospheric Trace Constituents," Proceedings of the 28th International Astrophysical Colloquium, "Our Changing Atmosphere," Leige, Belgium, June 1989.
54. Kaye, J. A., R. B. Rood, D. J. Allen, E. M. Larson, and C. H. Jackman, "Three Dimensional Simulation of Spatial and Temporal Variability of Stratospheric Hydrogen Chloride," Geophys. Res. Lett., (accepted), 1989.

Interpretation of Satellite and In Situ Aerosol and Trace Gas Data using Chemical-Dynamical Models.

Principal Investigator: Ronald G. Prinn, MIT, Cambridge, MA 02139

Objectives: We utilize global 3D chemical-dynamical-radiative models, analytical dispersion models, and statistical theory to address: (a) interpretation of recent satellite and in situ data on stratospheric aerosols which play important roles in the global energy budget and in the stratospheric sulfur cycle; (b) interpretation of satellite and in situ data on several trace gases of importance to our understanding of the chemistry of the stratospheric ozone layer; and (c) better definition of the spatial and temporal resolution required for determination of ozone trends from a network of ozone-sonde or lidar stations. The satellite data of interest come from NIMBUS-7 (SAMS, SAM II, LIMS), SAGE-1 and SME. The in situ data come from balloons, aircraft, and ground-based observations (including the Global Atmospheric Gases Experiment – GAGE).

Summary of 1988-1989 progress:

A critical examination of ozone variability and instrumental precision indicates that the current ozonesonde network is insufficient to detect a trend in tropospheric ozone of $\leq 1\%$ per year at the 2σ level even at stations with records a decade in length. We have concluded that in order to detect a 1% per year trend in a decade or less it will be necessary to decrease the time between observations from its present value of 3-7 days to 1 day or less. We have developed an analytical theory taking into account photochemistry, surface deposition, and wind climatology to define the "effectively sampled region" for an observing station which forms the basis for defining a suitable global network for determining regional and global ozone trends; a paper describing the work has been published (Prinn, 1988a).

We have also completed a detailed review of atmospheric halocarbons (CF_2Cl_2 , CH_3Cl , CCl_3F , CH_3CCl_3 , CCl_4 , CHClF_2 , CF_4 , $\text{C}_2\text{Cl}_3\text{F}_3$, CH_3Br , CBrClF_2 , CH_3I) and products of halocarbon decomposition (HCl , HF , ClO , ClONO_2) with the goal of identifying major shortcomings and/or contradictions in the available data. Largest trends are seen for CHClF_2 and $\text{C}_2\text{F}_3\text{Cl}_3$ but absolute calibration and global emission estimates for these 2 species are very uncertain. Also data on the stratospheric trends in HCl , ClO , and ClONO_2 are uncertain or nonexistent and the trends that have been reported for HF are not consistent with trends in their fluorocarbon sources. This work has also been published (Prinn, 1988b).

The annual percentage increases in concentrations of the chlorofluorocarbons $\text{CF}_2\text{ClCFCl}_2$ (CFC-113, an industrial solvent) and CHClF_2 (CFC-22, a refrigerant) are the highest among major chlorofluorocarbons in the atmosphere today. We have computed the present-day atmospheric lifetimes for these species using our global three-dimensional dynamical-chemical model. The present-day lifetimes of both are long (15.5 years for CHClF_2 , and 136 or 195 years for $\text{CF}_2\text{ClCFCl}_2$ depending on assumed O_2 absorption cross-sections) underscoring the need to decrease their emissions in order to minimize their future role in ozone destruction and greenhouse warming. These results have been published (Golombek and Prinn, 1989a).

The compound 1,1-dichloro-2,2,2-trifluoroethane (CHCl_2CF_3 ; CFC-123) is a proposed replacement for trichlorofluoromethane (CFCl_3 ; CFC-11). We have computed the chemical destruction rates by various mechanisms and the steady-state lifetime of CFC-123 using our global three-dimensional chemical-dynamical model. The major destruction mechanism for this species is reaction with the hydroxyl radical in the troposphere below the altitude of 12 km which accounts for 89% of its total loss rate. The computed steady-state lifetime for CFC-123 is 1.87 ± 0.07 years (1σ) which is very much shorter than that for CFC-11 which is destroyed largely in the stratosphere. For equal mass emission rates of CFC-123 and CFC-11 into the atmosphere, the steady-state atmospheric content and steady-state injection rate of chlorine into the stratosphere are respectively 35 and 15 times less for CFC-123 than for CFC-11. A paper on this work by Prinn and Golombek has been submitted to *Nature*.

We have also studied the processes maintaining the non-volcanically-perturbed stratospheric sulfuric acid (Junge) layer using our global three-dimensional model. The model includes production of SO_2 from OCS, oxidation of SO_2 to gaseous H_2SO_4 , condensation-evaporation equilibrium of gaseous and particulate H_2SO_4 , condensation growth of particulates as they enter the tropopause-upper troposphere region, and particle rainout in the lower troposphere. We have compared our results with the NIMBUS 7 SAM II and AEM-2 SAGE stratospheric aerosol extinction data for periods when the stratosphere was not perturbed by recent volcanic eruptions. The model simulates the general behavior of stratospheric aerosol extinction including the existence of a polar tropopause enhancement in this extinction. Agreement is good in the tropics but there is a tendency however for the model in high latitudes to overpredict aerosol extinction above 15 km due perhaps to an overly vigorous predicted circulation or to inadequate knowledge of particle sizes. We identify two major non-volcanic sources for stratospheric H_2SO_4 : one is upwardly transported and photodissociated OCS and the other is upwardly transported SO_2 . The importance of SO_2 is a new and significant result. A paper on this work by Golombek and Prinn has been submitted to the *Journal of Atmospheric Chemistry*.

Publications:

1. Prinn, R. (1988a). Toward an improved global network for determination of tropospheric ozone climatology and trends. *J. Atmos. Chem.*, 6, 281-298.
2. Prinn, R. (1988b). How have the atmospheric concentrations of the halocarbons changed? In "The changing Atmosphere" (ed. S. Rowland and I. Isaksen, J. Wiley and Sons Ltd.) pp. 33-48.
3. Golombek, A., and R. Prinn (1989). Global 3-dimensional model calculations for the budgets and present-day atmospheric lifetimes of $\text{CF}_2\text{ClCFCl}_2$ (CFC-113) and CHClF_2 (CFC-22). *Geophys. Res. Lett.*, in press for October 1989 issue.

B. MODELLING PHOTOCHEMICAL PROCESSES

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A. Studies of Stratospheric Particulates (Task 673-62-13-20)

B. Investigators and Institutions:

P.I. Dr. Owen B. Toon, Earth System Science Division, NASA Ames Research Center, Moffett Field Ca.

Co. I. Prof. Richard Turco, Dept. of Atmospheric Science, University of California, Los Angeles, Ca.

Co. I. Prof. Patrick Hamill, Dept. of Physics, San Jose State University, San Jose, Ca.

Co. I. Prof. Gary Thomas, Dept. of Astrophysical, Planetary and Atmospheric Studies, U. Colorado, Boulder Co.

C. Research Objectives:

The principal objective of this work is to quantify the importance of heterogeneous chemistry to ozone depletion in the polar regions. The ambient stratospheric sulfate layer, and especially clouds in the polar stratosphere may provide surfaces upon which reactions occur and they may sequester or remove materials from the stratosphere. Our goals are to theoretically simulate such heterogeneous processes so that we may better quantify their importance, and so that we can identify processes that need to be studied in the laboratory. A sophisticated computer model of polar stratospheric clouds has been developed and used to study the properties of ice clouds. The model has recently been extended to investigate nitric acid clouds and ice clouds as well as their interactions with stratospheric gases. The model is now being applied to interpret data collected during recent expeditions to the Antarctic and the Arctic. Some work has also been done to understand the properties of noctilucent clouds and their implications for the chemistry and dynamics of the upper stratosphere.

D. Progress and Results:

A sophisticated numerical model of cirrus cloud microphysics has been developed and simulations of water ice clouds in the Antarctic atmosphere have been conducted. One conclusion of this work is that the particle sizes, optical depths and vertical mass transfer rates of ice

clouds are very sensitive to the cooling rates at which these clouds form. We also concluded that nitric acid is not incorporated into ice clouds by physical processes such as nucleation or coagulation, but rather by vapor transfer processes. We have also developed a theory which allows us to relate laboratory measurements of heterogeneous reaction rates to the reactions which occur on particle surfaces. We have additionally developed a theory for the vapor pressures of nitric acid trihydrate which seems to explain most of the laboratory data. We have analyzed data obtained during the Antarctic Ozone expedition and shown that the polar clouds that are present much of the time are not composed of water ice, but are composed of condensed nitric acid. We have recently improved the cloud model by treating nitric acid, hydrochloric acid and other condensed phase materials as minor constituents within ice and nitric acid particles. We are currently adding a gas phase chemistry package to the cloud model. This work will allow us to study more precisely how the ice clouds interact with the chemistry in the polar night. We have found that the brightness of noctilucent clouds is very sensitive to the supply of water vapor. Therefore, we have suggested that the production of water due to the rise of methane in the atmosphere over the last century is what allows these clouds to be observed so frequently now, when they were never reported until the end of the last century. We have also shown that the brightness of the clouds may vary diurnally in response to a diurnal tide, explaining a brightness difference between ground based and satellite observations which were taken at different times of day.

E. Journal Publications: P.Hamill, R.P. Turco, and O. B. Toon, On the Growth of Nitric and Sulfuric Acid Aerosol Particles Under Stratospheric Conditions, *J. Atmos. Chem.* 7, 287-315 (1988). G.E. Thomas, J.J. Olivero, E. J. Jensen, W. Schroeder, and Owen B. Toon, Relation Between Increasing Methane and the Presence of Ice Clouds at the Mesopause. *Nature*, 338,490-492,(1988). O.B. Toon, et al., Physical Processes in Polar Stratospheric Ice Clouds. *J. Geophys.*,in Press (1988).R.P. Turco, O.B. Toon,P. H. Hamill, Heterogeneous Physicochemistry of the Polar Ozone Hole, *J. Geophys. Res.* in press (1989). S. Kinne, O. B. Toon, G.C. Toon, C.B. Farmer, Measurements of the Size and Composition of Particles in Polar Stratospheric Clouds from Infrared Solar Absorption Spectra, *J. Geophys. Res.* in press (1989).

A. Title of Research Task:

Homogeneous and Heterogeneous Chemistry along Air Parcel Trajectories

B. Investigators:

R. L. Jones, U. K. Meteorological Office, Bracknell, Berkshire, UK
 D. L. McKenna, U. K. Meteorological Office, Bracknell, Berkshire, UK
 L. R. Poole, NASA Langley Research Center, Hampton, VA
 S. Solomon, NOAA Aeronomy Laboratory, Boulder, CO

C. Research Objectives:

The goal of the present research was to study the coupled heterogeneous and homogeneous chemistry due to polar stratospheric clouds (PSC's) using Lagrangian parcel trajectories for interpretation of the Airborne Arctic Stratosphere Experiment (AASE). This approach represents an attempt to quantitatively model the physical and chemical perturbations to stratospheric composition due to formation of PSC's using the fullest possible representation of the relevant processes. Further, the meteorological fields from the UK Met. office global model were used to deduce potential vorticity and inferred regions of PSC's as an input to flight planning during AASE.

D. Summary of Progress and Results

Potential vorticity and inferred PSC maps were made available daily during the AASE mission. In most cases, the inferred PSC's coincided well with those observed and were therefore useful in flight planning.

A detailed cloud microphysics model was coupled to the Lagrangian photochemistry model prior to the AASE mission. The coupled model was implemented on a microvax computer and was run in real time during the field experiment.

The model was used to interpret a great deal of the AASE data. Particular success was achieved for the flight of January 24, 1989. During this period, synoptic scale forcing in the troposphere led to rapid stratospheric cooling above Scandanavia with subsequent PSC cloud formation. The ER-2 sampled air within the cloud during its formation stages. Model calculations of the evolution of cloud particle growth (Poole et al., 1989) and chemical composition (Jones et al., 1989) were in remarkable agreement with observations. The calculated particle volume agreed well with measurements of particles from the ER-2, and the associated production of ClO appeared to be in very good agreement with the model estimates. This cloud event therefore represented an excellent test of current understanding of cloud microphysics and heterogeneous chemistry for a case of relatively rapid cooling.

Heterogeneous chemistry plays a critical role in determining the abundance of reactive nitrogen, which can in turn affect ClO through formation and destruction of the ClONO₂ reservoir long after exposure to PSC's. Thus, observations of ClO place important constraints on the abundances of stratospheric NO and NO₂. During some flights, ClO abundances of only a few parts per trillion by volume were observed at ER-2 flight levels, in contrast to levels above a part per billion in heavily processed air. The range of ClO abundance depends on many factors including cloud processing, solar zenith

angles, and availability of reactive nitrogen. Trajectory studies can be used to evaluate the first two factors and hence to deduce information about the reactive nitrogen abundances (Solomon et al., 1989).

Many of the AASE flights revealed a general 'dog-dish' structure in ClO, with relatively low values at lower latitudes followed by a maximum near 65-70N, followed by lower values at higher latitudes. Modeling studies showed that this structure is due to the combined effects of processing of air parcels within PSC's coupled with solar zenith angle effects. In particular, heavily processed air at high latitudes displays relatively little ClO due to the large solar zenith angles present there, favoring the ClO dimer as the dominant reservoir for the liberated chlorine. At lower latitudes, solar zenith angles are smaller, favoring ClO over the dimer, but PSC processing is limited. Thus, a maximum in ClO abundance is found at an intermediate latitude region where solar illumination and cloud processing overlap most effectively.

Detailed studies were carried out to evaluate the ozone destruction before, during and post-mission (McKenna et al., 1989). These studies were based largely on ensembles of representative trajectories at various latitudes. For the period of the mission, careful attention was paid to the AASE data, which place important constraints on the available reactive chlorine and nitrogen and hence on ozone depletion.

E. Journal Publications

Jones, R. L., D. L. McKenna, L. R. Poole, and S. Solomon, in preparation for submission to *Geophys. Res. Lett.*, 1989.

McKenna, D. L., R. L. Jones, L. R. Poole, and S. Solomon, in preparation for submission to *Geophys. Res. Lett.*, 1989.

Poole, L. R., S. Solomon, D. L. McKenna, and R. L. Jones, in preparation for submission to *Geophys. Res. Lett.*, 1989.

Solomon, S., R. L. Jones, D. L. McKenna, and L. R. Poole, in preparation for submission to *Geophys. Res. Lett.*, 1989.

UATDAP Research Summary 1988

A. Title of Research Task

Study of Ozone Observations

B. Investigators and Institutions

Dr. Mark Allen
Earth and Space Sciences Division
Jet Propulsion Laboratory
California Institute of Technology
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C. Abstract of Research Objectives

For the purpose of testing the adequacy of current models of atmospheric chemistry, one dimensional (1D) model calculations have been compared with vertical ozone profiles derived from ground-based diurnal radio measurements.

D. Summary of Progress and Results

One dimensional model calculations accurately reproduce the relative diurnal variation of mesospheric ozone at equinox, suggesting that the model value of the ozone photolysis rate coefficient is accurate to better than 10%. Various changes in model parameters, previously suggested to better reproduce the ozone abundance vertical profile, result in only small differences in the relative diurnal variation, indicating that these observations do not provide a sensitive test of the mesospheric chemistry controlling the abundance of odd oxygen.

E. Journal Publications

W. C. Zommerfelds, K. F. Kunzi, M. E. Summers, R. M. Bevilacqua, D. F. Strobel, M. Allen, and W. J. Sawchuck. Diurnal Variations of Mesospheric Ozone Obtained by Ground-based Microwave Radiometry. *J. Geophys. Res.*, in press (1989).

Theoretical Studies of Stratospheric Chemistry

NAGW-1230

Principal investigators: M. B. McElroy and S. C. Wofsy

Abstract

The research focussed on elucidating important aspects of stratospheric chemistry, with emphasis on the stratosphere at high latitude and on interpretation of recent satellite observations from ATMOS and SAGE II. The role of heterogeneous processes was examined using data from the laboratory and from recent aircraft experiments in the Antarctic and the Arctic.

Summary of progress and results

Observations of O_3 declines over Antarctica, in combination with measurements of ClO and BrO free radicals, provide the information required to test models of the processes responsible for O_3 loss. Analysis of observations in the Antarctic stratosphere indicated that 60–70% of the observed loss of O_3 was accomplished by reactions of ClO and BrO radicals. Formation of $(ClO)_2$ accounted for about three times the loss associated with reactions involving ClO and BrO. We examined possible additional pathways for ozone recombination, to try to explain the "missing" losses. We found that almost all candidate processes could be rejected after careful analysis of laboratory experiments. Two processes were identified that should be followed up by laboratory studies.

We took part in the Arctic Airborne Ozone Experiment in Stavanger, Norway. In association with the experimenters in this mission, we examined the processes responsible for denitrifying the atmosphere, analyzed the global conversion of N_2O to NO_y , and developed a method for reconstructing 3-dimensional tracer fields (e.g. NO_y , inorganic chlorine) using meteorological data in combination with limited *in situ* data.

The results show that the signature of formation of polar stratospheric clouds is consistent with thermodynamic data for $HNO_3 \cdot 3H_2O$. Denitrification appears to proceed rapidly once the atmosphere is cooled to the frost point temperature, and we argue that the process is enhanced by prior formation of a bi-modal distribution for $HNO_3 \cdot 3H_2O$ particles, as observed by the ER-2 and balloon sondes. The microphysical processes that give rise to the formation of a bimodal distribution remain unclear, an issue we are actively pursuing.

PUBLICATIONS

Chemistry of OClO in the Antarctic Stratosphere: Implications for Bromine, by R. J. Salawitch, S. C. Wofsy and M. B. McElroy, *Planet. Space Sci.*, 36, 213-224 (1988).

Interactions between HCl, NO_x , and H_2O ice in the Antarctic Stratosphere: Implications for ozone, by S. C. Wofsy, M. J. Molina, R. J. Salawitch, L. E. Fox, and M. B. McElroy, *J. Geophysical Research*, 93, 2442 - 2450 (1988).

Chemistry of the Antarctic Stratosphere, by M. B. McElroy, R. J. Salawitch, and S. C. Wofsy, *Planet. Space Sci.*, **36**, 73-87 (1988).

Influence of Polar Stratospheric Clouds on the Depletion of Antarctic Ozone, by R. J. Salawitch, S. C. Wofsy and M. B. McElroy, *Geophysical Research Letters*, **15**, 871-874 (1988).

Denitrification in the Antarctic Stratosphere, R. J. Salawitch, G.P. Gobbi, S. C. Wofsy, and M. B. McElroy, *Nature* **339**, 525-527 (1989).

Changing composition of the global atmosphere, M. B. McElroy and R. J. Salawitch, *Science* **243**, 763-770 (1989).

The challenge of global change, M. B. McElroy, *New Scientist*, 28 July 1988.

Studies of Polar Ice: Insights for atmospheric chemistry, M. B. McElroy, in *The environmental record in glaciers and ice sheets*, eds H. Oeschger and C. C. Langway, pp 363-377 (1989.)

Theoretical Modelling and Meteorological Analysis for the AASE Mission

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Abstract:

Objective is to provide real time constituent data analysis and potential vorticity computations in support of the Airborne Arctic Stratospheric Experiment (AASE). NMC meteorological data and potential vorticity computations derived from NMC data are projected onto aircraft coordinates and provided to the investigators in real time. ER-2, balloon and satellite constituent data is composited into modified Lagrangian-mean coordinates. Various measurements are intercompared, trends deduced and reconstructions of constituent field performed.

Summary of Progress and Results:

The real time data objectives were met during the Norway AASE mission and meteorological data files were provided to the investigators in Norway. Improvements in the analysis were made after the mission, and updated files have been provided to the archive at NASA Ames. Demand for the data sets has been high as the meteorological data has been crucial in determining the location of the polar vortex and interpreting the DC-8 column constituent data. Meteorological data analysis is now being extended to cover the previous AAOE mission period (August-September, 1987) so that potential vorticity data sets will be available for both missions.

The reconstruction and modified Lagrangian mean transformation procedure has proven to be a powerful tool for the extension and intercomparison of constituent data sets. Recently the DIAL lidar, ER-2 insitu and ozonesonde measurements taken at different locations have been directly compared with suprisingly good agreement.

In addition to this work, analysis of meteorological and total ozone data projects have continued. This analysis includes characterizing the effect of the QBO in modulating the Antarctic ozone depletion, comparison between the 1988 and 1987 southern hemisphere depletions, and analysis of long term trends

in ozone and temperature from NMC data. Additional research on gravity wave propagation and breakdown has also been performed.

Publications:

Antarctic springtime ozone depletion computed from temperature observations, J. E. Rosenfield, M. R. Schoeberl, and P. A. Newman, J. Geophys. Res., 93, 3833-3849, 1988.

The morphology and meteorology of southern hemisphere spring total ozone mini-holes, P. A. Newman, L. R. Lait, and M. R. Schoeberl, Geophys. Res. Lett., 15, 923-926, 1988.

Effect of self-consistent horizontal diffusion coefficients on 2-dimensional N₂O model distributions, C. H. Jackman, P. A. Newman, P. D. Guthrie, and M. R. Schoeberl, J. Geophys. Res., 93, 5213, 1988.

The role of gravity wave generated advection and diffusion in transport of tracers in the mesosphere, J. R. Holton and M. R. Schoeberl, in press, J. Geophys. Res., 1988.

Mixing rates calculated from potential vorticity, P. A. Newman, M. R. Schoeberl, R. A. Plumb, and J. E. Rosenfield, J. Geophys. Res., 93, 5221, 1988.

Reply to Elliot and Rowland, M. R. Schoeberl and R. S. Stolarski, Geophys. Res. Lett., 15, 198-199, 1988.

Breakdown of vertically propagating gravity waves forced by orography, J. T. Bacmeister and M. R. Schoeberl, J. Atmos. Sci., 46, 2109-2134, 1989.

The 1988 Antarctic ozone depletion: Comparison with previous year depletions, M. R. Schoeberl, R. S. Stolarski, and A. J. Krueger, Geophys. Res. Lett., 16, 377-380, 1989.

Quasi-biennial modulation of the Antarctic ozone depletion, L. R. Lait, M. R. Schoeberl, and P. A. Newman, J. Geophys. Res., 1989.

Reconstruction of the constituent distribution and trends in the Antarctic polar vortex from ER-2 flight observation, M. R. Schoeberl, L. R. Lait, M. Proffitt, P. A. Newman, R. L. Martin, D. L. Hartmann, M. Loewenstein, J. Podolske, S. E. Strahan, J. Anderson, K. R. Chan, B. Gary, J. Geophys. Res., in press, 1989.

Potential vorticity estimates in the south polar vortex from ER-2 flight data, D. L. Hartmann, K. R. Chan, B. L. Gary, M. R. Schoeberl, P. A. Newman, R. L. Martin, M. Loewenstein, J. R. Podolske, S. E. Strahan, J. Geophys. Res., 1989.

Evidence of the mid-latitude impact of Antarctic ozone depletion, R. J. Atkinson, W. A. Mathews, P. A. Newman, R. A. Plumb, Nature, 340, 290-294, 1989.

THE INTERACTION OF SOLAR ULTRAVIOLET RADIATION (280-400 NM)
WITH THE TERRESTRIAL SYSTEM

PRINCIPAL INVESTIGATOR: John E. Frederick
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RESEARCH OBJECTIVES:

This research is devoted to examining the role of the stratosphere, and to a lesser extent the troposphere, in determining the ultraviolet radiation levels incident on the biosphere. The approach combines radiative transfer calculations (which include multiple Rayleigh scattering, absorption by an arbitrary number of gases, scattering within clouds, and reflection from a lower boundary) with measurements of atmospheric composition.

PROGRESS AND RESULTS (1988-89):

Results published in 1988 showed that variations in local cloudiness of plus or minus 10% at middle latitudes could lead to changes in surface ultraviolet radiation as great as those predicted from trends in ozone since 1970. Analyses performed for the Scientific Assessment of Stratospheric Ozone: 1989 demonstrate that trends in ozone of the magnitude derived from Dobson measurements would not appear in a straightforward manner in the data record acquired by the Robertson-Berger (RB) meter network. There is therefore no inconsistency between the derived decline in ozone over middle latitudes of the Northern Hemisphere and the failure of the RB meters to observe increased ultraviolet irradiance at the ground. Effects of local cloudiness and of localized sources of air pollution can be major factors in determining trends in the RB meter output.

In other research supported under this grant we examined the impact of the springtime Antarctic ozone depletion on the surface ultraviolet radiation environment of the region. As one proceeds from September through December surface radiation level increase in response to the natural change in solar elevation. However, the presence of a large ozone depletion in October leads to ultraviolet irradiances similar to or greater than those at summer solstice. The

effect of the ozone hole is therefore to extend the duration of summerlike ultraviolet radiation levels. Any persistence of the ozone depletion as summer approaches would be especially significant here.

JOURNAL PUBLICATIONS (1988-89):

Frederick, J. E., and D. Lubin, The budget of biologically active ultraviolet radiation in the earth-atmosphere system, J. Geophys. Res., 93, 3925-3832, 1988.

Frederick, J. E., and H. E. Snell, Ultraviolet radiation levels during the Antarctic spring, Science, 241, 438-440, 1988.

Lubin, D., J. E. Frederick, and A. J. Krueger, The ultraviolet radiation environment of Antarctica: McMurdo Station during September-October 1987, J. Geophys. Res., 94, 8491-8496, 1989.

Research Summary (1988)

A. Title of Research Task:

A Correlative Study of SME Ozone Observations and Ground-based Microwave Water Vapor Measurements

B. Investigators and Institutions:

Principal Investigator: Richard M. Bevilacqua
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C. Abstract of Research Objectives:

The major objective of the study is to employ Solar Mesosphere Explorer (SME) ozone and solar flux measurements, along with ground-based microwave water vapor measurements, in order to study the photochemistry of the mesosphere. Water vapor is the climatological variable most important in controlling ozone concentrations in the mesosphere because it is the predominant source of odd hydrogen which (through the odd hydrogen catalytic cycle) dominates ozone loss in the mesosphere. By analysis of the water vapor and ozone data, and interpretation with a 1-D photochemical model, we intend to provide a more complete understanding of the vertical distribution of ozone in the mesosphere. In addition, the measured water vapor profiles will be used with the 1-D model to investigate vertical transport processes and time-scales in the mesosphere.

D. Summary of Progress and Results:

We have analyzed three years of ground-based microwave water vapor measurements obtained at Penn State. The observations indicate that the seasonal variation of water vapor in the upper mesosphere is dominated by an annual variation with low abundances in winter and high abundances in summer. This suggests that advection dominates diffusion in establishing the vertical distribution of water vapor in the mesosphere, and is consistent with the steep vertical gradient in the water vapor mixing ratio profile persistently observed in the upper mesosphere. However, it is very difficult to reconcile the annual water vapor variation with the predominantly semiannual variation of ozone in the upper mesosphere observed by SME. In fact, we have performed

a series of 1-D photochemical model calculations which verify that (within the context of the hydrogen/oxygen chemistry considered in the model), the seasonal variation of water vapor cannot be the mechanism for the semiannual ozone variation. This variation is either a manifestation of some heretofore unknown photochemical mechanism; or, it could be driven by a seasonal variation in the vertical transport of atomic oxygen from the thermosphere.

We have also modeled the diurnal variation of ozone in the mesosphere and compared this to measurements made by ground-based microwave techniques at Bern Switzerland in the winter and spring of 1987. We find that the 1-D model calculations accurately reproduce the relative diurnal ozone variation at equinox, suggesting that the ozone photolysis rate coefficient is accurate to better than 10%. However, in winter the model underpredicts the observed relative diurnal variation by a factor of 2, with the major part of this discrepancy resulting from the observed post midnight increase in ozone which is not obtained in the model.

Finally, we have used our 1-D photochemical model, along with a time-dependent heat equation, to study the response of mesospheric ozone concentrations to short-term uv solar flux variations. The model results have been compared with the observed ozone response obtained from a statistical analysis of SME ozone measurements. We find that the model with sinusoidal forcing of mesospheric chemistry by solar uv flux variations with a period of 27 days, combined with temperature-chemistry feedback and time dependent atmospheric temperature effects, reproduces the major characteristics of the observed ozone response. However, we also find that the magnitude of the computed ozone response in the upper mesosphere (above 70 km) to increased solar uv flux is strongly coupled to the water vapor abundance through the odd hydrogen catalytic cycle which removes ozone. Therefore, as a consequence of the observed seasonal variation of water vapor in the upper mesosphere, we predict a significant seasonal variation of the magnitude of the ozone response to solar uv flux variations.

E. Journal Publications:

- 1) Bevilacqua, R. M., J. J. Olivero, and C. L. Croskey, Mesospheric water vapor measurements from Penn State: monthly mean observations (1984-1987), J. Geophys. Res., in press, 1989.
- 2) Zommerfelds, W. C., K. F. Kunzi, M. E. Summers, R. M. Bevilacqua, D. F. Strobel, M. Allen, and W. J. Sawchuck, Diurnal variations of mesospheric ozone obtained by ground-based microwave radiometry, J. Geophys. Res., in press, 1989.
- 3) Bevilacqua R. M., D. F. Strobel, M. E. Summers, J. J. Olivero, and M. Allen, The seasonal variation of water vapor and ozone in the upper mesosphere: implications for vertical transport and ozone photochemistry, J. Geophys. Res., submitted, 1989.
- 4) Summers, M. E., R. M. Bevilacqua, D. F. Strobel, M. T. DeLand, M. Allen, and G. M. Keating, A model study of the response of mesospheric ozone to short-term solar ultraviolet flux variations, J. Geophys. Res., submitted, 1989.

C. STRATOSPHERIC DYNAMICS

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Biennial Research Summary

- A. **Title:** Transport and Circulation of the Middle Atmosphere
- B. **Investigators and Institutions:** Conway B. Leovy, Institute for Environmental Studies, University of Washington, Seattle, Wa, 98195
- C. **Abstract of Research Objectives:** The objective of this research program is to improve our understanding of large scale circulation and transport processes in the stratosphere and mesosphere by means of diagnostic analyses of spacecraft and in situ data together with modeling. Particular emphasis is placed on the mechanisms for interannual variability of temperature, wind, and ozone concentration, and on the mechanisms of trace species transport.
- D. **Summary of Progress and Results:** (1) A diagnostic study of seasonal and interannual variations of temperature and ozone from the tropopause to the mesopause using data from the Nimbus 7 LIMS, SCR, and SBUV instruments and SME airglow data (Sun and Leovy, 1989). Mechanisms responsible for driving the semiannual oscillation were identified. The relationship between the semiannual and quasiannual oscillations was documented. (2) An analysis of the distribution of cross-isentropic transport of ozone and potential vorticity in relation to winter warming events has been completed and is in preparation for publication. (3) Identification of Hough mode components of diurnal temperature variations in LIMS data has been completed. (4) Improvements in our diabatic model to allow more accurate calculations in the Antarctic and Arctic lower stratospheres, including aerosol emission and scattering, is underway and nearing completion.
- E. **Journal Publications:** C.-R. Sun and C. Leovy, Ozone Variability in the Equatorial Middle Atmosphere. J. Atmos. Sci., (in press, 1989).

Report to NASA Upper Atmosphere Research Program

Research Summary for 1988 - 1989

TITLE: Wave Dynamics and Transport in the Stratosphere

PRINCIPAL INVESTIGATOR: Professor J. R. Holton, University of Washington

ABSTRACT: This grant supports a program of theoretical studies, numerical modeling, and data analysis designed to elucidate the dynamics of large scale motions in the stratosphere and their roles in the transport of heat, momentum, and trace chemical substances. The emphasis of the project is on the physics of wave motions and the role of wave, mean-flow interactions in maintaining the observed heat, momentum, and trace species budgets.

SUMMARY OF PROGRESS 1987 - 1988

i) Wave, mean-flow interactions in the stratosphere:

An 18 year record of gridded NMC data for the Northern Hemisphere stratosphere was used to study the spatial variability of planetary wave activity in the stratosphere as well as the longitudinal dependence of tropospheric forcing. Mapped fields of the Ertel Potential Vorticity were used to derive an index of planetary wave-breaking events. Such events were then related to the occurrence of sudden warmings. The result is a climatology of the stratospheric polar vortex, and the role of wavebreaking in vortex erosion. The differences between cold undisturbed winters and active winters with sudden warmings are clearly revealed by the combination of the wavebreaking index and the vortex area index.

ii) The effect of orographic forcing on the mean flow of the stratosphere: We investigated the role of tropospheric forcing in determining the climatology of the Northern Hemisphere winter stratosphere using the NCAR Community Climate Model to determine the sensitivity of the mean flow of the stratosphere to orographically forced planetary waves in the troposphere. Seven model cases, distinguished by differing amplitudes of orography, were each integrated for 360 days under perpetual January conditions. Contrary to expectations, the time-averaged stratospheric jet weakened nearly monotonically with increased orography in the model. Furthermore, the fraction of wave activity transmitted through the lower stratosphere was rather independent of orography. It is clear from the analysis of these simulations that larger amplitude orography indeed generally forces weaker zonal flow in the stratosphere. The hypothesis that the stratosphere independently vacillates between two states is not verified by this experiment. Most of the transience in the stratospheric zonal flow can be directly attributed to transience in the planetary wave flux emanating from the troposphere. There is evidence of the hypothesized vacillation in the CCM, but only when the troposphere and stratosphere are considered together as a single system.

iii) Tracer experiments with the NCAR CCM

We have developed an "off line" chemical tracer model that utilizes 6 hour averaged velocity data from the CCM in order to advect a long-lived chemical tracer. A zonal mean global distribution of N₂O for September, based on SAMS satellite data, was used to initialize the tracer model and the model is run through an annual cycle. The overall simulation shows very good agreement with the satellite observations. The results were used to investigate short time scale tracer variance statistics.

iv) The role of gravity waves in circulation and transport in the mesosphere:

Traditionally, models of the vertical profiles of long-lived mesospheric tracers such as water vapor and carbon monoxide have assumed that vertical transport due to

diffusion by small scale turbulence balanced the chemical sources and sinks. A test of the comparative roles of advection and diffusion in the mesosphere has been made with a zonally symmetric model of the global mesosphere, employing Lindzen's wavebreaking parameterization.

v) Transport circulation deduced from SAMS tracer data

The Stratospheric and Mesospheric Sounder (SAMS) instrument on the Nimbus 7 satellite provided about 3 years of data on the zonal mean distributions of N_2O and CH_4 in the stratosphere. These data were utilized to investigate the annual and semiannual cycles in long-lived tracer mixing ratio distributions. The tracer continuity equation was solved diagnostically to obtain the effective transport velocity (i. e., the meridional circulation that could produce the observed seasonal variations in the tracer fields). The resulting circulation was qualitatively in agreement with the diabatic circulation derived by other workers. However, the transport circulation exhibits a stronger equinoctial subsidence in the equatorial upper stratosphere, as required to produce the observed "double peak" structure in the tracer distribution at low latitudes.

JOURNAL PUBLICATIONS 1988 - 1989

Baldwin, M. P., and J. R. Holton, 1988: Climatology of the stratospheric polar vortex and planetary wave breaking. *J. Atmos. Sci.*, **45**, 1123-1142.

Holton, J. R., and W. K. Choi, 1988: Transport circulation deduced from SAMS trace species data. *J. Atmos. Sci.*, **45**, 1929-1939.

Holton, J. R., and M. R. Schoeberl, 1988: The role of gravity wave generated advection and diffusion in transport of tracers in the mesosphere. *J. Geophys. Res.*, **93**, 11,075-11,082.

Robinson, W. A., 1987: Two applications of potential vorticity thinking. *J. Atmos. Sci.*, **44**, 1554-1557.

Robinson, W. A., 1988: Analysis of LIMS data by potential vorticity inversion. *J. Atmos. Sci.*, **45**, 2319-2342.

Robinson, W. A., 1988: Irreversible wave-mean flow interactions in a mechanistic model of the stratosphere. *J. Atmos. Sci.*, **45**, 3413-3430.

O'Sullivan, D., 1988: Rossby wave propagation on beta-planes. *J. Atmos. Sci.*, **45**, 41-54.

Yoden, S., 1987a: Bifurcation properties of a stratospheric vacillation model. *J. Atmos. Sci.*, **44**, 1723-1733.

Yoden, S., 1987b: A new class of stratospheric vacillations in a highly truncated model due to wave interference. *J. Atmos. Sci.*, **44**, 3696-3709.

Yoden, S., and J. R. Holton, 1988: A new look at equatorial quasi-biennial oscillation models. *J. Atmos. Sci.*, **45**, 2703-2717

A. Dynamical Meteorology of the Equatorial and Subtropical Stratosphere

B. *Timothy J. Dunkerton, Principal Investigator*

Donald P. Delisi

Mark P. Baldwin

C. RESEARCH OBJECTIVES

This observational and theoretical study seeks to examine and explain the large-scale motions of the tropical and subtropical stratosphere and their interaction with the extratropical atmosphere. Upper air data, together with satellite data sets and global analyses, are being used to investigate the climatological behavior of the stratosphere and departures from climatology in large-amplitude wave events. Theoretical models are being developed and used to investigate the mean meridional circulation of the middle atmosphere and the role of gravity and planetary wave transport in the zonally averaged circulation.

D. PROGRESS SUMMARY

Nimbus 7 SAMS and LIMS data were used to investigate the seasonal variation of the stratopause semiannual oscillation (SAO). It was found that the first semiannual cycle in the year is much stronger, in both easterly and westerly phase, than the second cycle. Strong tropical-polar connections were also evident in the data, suggesting that stratospheric warmings in the high-latitude winter affect the timing and magnitude of SAO phase onset. During summer 1982, an effect of the El Chichón eruption was documented, including (in addition to the well-known warming of the tropical lower stratosphere) a cooling of the upper stratosphere and intensification of the Hadley circulation. Upper air data have been processed into time series form and the spectra of equatorial and planetary Rossby wave activity are currently being investigated. NMC analyses have been used to document the earliest major warming of the Northern hemisphere winter (December 1987), showing that an anomalous tropospheric forcing was responsible for the warming event. A complete NMC Northern hemisphere climatology of ultra-long planetary waves has been created and used to demonstrate that anomalous tropospheric conditions (persistent anomalies and large-scale displacement of the entire tropospheric vortex) are both necessary and sufficient for the occurrence of large-amplitude stratospheric wave events in winter.

A high-resolution two-dimensional model of the troposphere and middle atmosphere has been developed and used to investigate the nonlinear Hadley circulation of the middle atmosphere, together with the dynamics of the quasi-biennial and semiannual oscillations. This model has demonstrated, among other things, that the stratosphere does not relax to radiative equilibrium when wave transport processes are removed. A theory of the single-cell, hemispherically-asymmetric nonlinear Hadley regime was developed, generalizing an earlier theory of the (nearly) symmetric two-cell Hadley circulation. Contraction of a nonlinear Hadley circulation, with wave momentum deposition outside the polar vortex, is likely to be important in the morphology of Southern hemisphere trace species.

E. JOURNAL PUBLICATIONS

- Dunkerton, T.J., 1988: Body force circulation and the Antarctic ozone minimum. *J. Atmos. Sci.*, **45**, 427-438.
- Dunkerton, T.J., 1989: Theory of internal gravity wave saturation. *Pure and Appl. Geophys.*, **130**, 373-397.
- Dunkerton, T.J., D.P. Delisi, and M.P. Baldwin, 1988: Distribution of major stratospheric warmings in relation to the quasi-biennial oscillation. *Geophys. Res. Lett.*, **15**, 136-139.
- Dunkerton, T.J., 1989: Body force circulations in a compressible atmosphere: key concepts. *Pure and Appl. Geophys.*, **130**, 243-262.
- Delisi, D.P., and T.J. Dunkerton, 1988: Equatorial semiannual oscillation in zonally averaged temperature observed by the Nimbus 7 SAMS and LIMS. *J. Geophys. Res.*, **93**, 3899-3904.
- Delisi, D.P., and T.J. Dunkerton, 1988: Seasonal variation of the semiannual oscillation. *J. Atmos. Sci.*, **45**, 2772-2787.
- Dunkerton, T.J., 1989: Nonlinear Hadley circulation driven by asymmetric differential heating. *J. Atmos. Sci.*, **46**, 956-974.
- Baldwin, M.P., and T.J. Dunkerton, 1989: The stratospheric major warming of early December 1987. *J. Atmos. Sci.*, to appear.
- Dunkerton, T.J., 1989: Eigenfrequencies and horizontal structure of divergent barotropic instability originating in tropical latitudes. *J. Atmos. Sci.*, submitted.
- Baldwin, M.P., and T.J. Dunkerton, 1989: Observations and statistical simulations of a proposed solar cycle/QBO/weather relationship. *Geophys. Res. Lett.*, **16**, 863-866.
- Gray, L.J., and T.J. Dunkerton, 1989: The role of the seasonal cycle in the quasi-biennial oscillation of ozone. *J. Atmos. Sci.*, submitted.
- Baldwin, M.P., 1989: An updated climatology of the northern hemisphere winter polar stratospheric vortex. *J. Atmos. Sci.*, in preparation.

CENTER FOR ATMOSPHERIC THEORY AND ANALYSIS

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October 16, 1989

RESEARCH SUMMARY

A. Grant Title: Irreversible Transport Associated with Planetary Waves

NASA Number: NAGW-772

CU Number: 1533103

B. Investigators: Murry L. Salby
Department of Astrophysical, Planetary,
and Atmospheric Sciences
University of Colorado
Boulder, CO

Rolando R. Garcia
National Center for Atmospheric Research
Boulder, CO

Susan Solomon
Aeronomy Lab/NOAA
Boulder, CO

C. Research Objectives: The proposed effort was to focus on horizontal air motions associated with planetary waves and the interaction between this form of transport and the global circulation and photochemistry in the stratosphere.

D. Progress: Eddy air motions have been investigated along several avenues. These include the development and diagnosis of an equivalent barotropic model which accurately represents column-integrated behavior and horizontal air motions, investigation of a nonlinear planetary wave critical layer as a paradigm of dispersive air motions in the stratosphere, a study of the competition between eddy transport and radiative drive in controlling the circulation and tracer distributions in the stratosphere, an investigation of the interaction between the quasi-biennial oscillation in the tropics and the extratropical circulation in the stratosphere, and an investigation of dynamically induced disturbances to the distribution and abundance of column ozone. In addition, studies of asynoptic sampling, of relevance to stratospheric problems and to climate in general, have been completed.

E. Publications:

Salby, M., 1988: Asynoptic sampling considerations for wide-field-of-view measurements of outgoing radiation. Part I: Spatial and temporal resolution. *J. Atmos. Sci.*, **45**, 1176-1183

_____, 1988: Asynoptic sampling considerations for wide-field-of-view measurements of outgoing radiation. Part II: Diurnal and random space-time variability. *J. Atmos. Sci.*, **45**, 1184-1204.

_____, 1989: Deep circulations under simple classes of stratification. *Tellus*, **41A**, 48-65.

October 16, 1989

- _____, 1989: Climate monitoring from space: Asynoptic sampling considerations. *J. Climate* (in press).
- _____, R. Garcia, D. O'Sullivan, and J. Tribbia, 1989: Global transport calculations with an equivalent barotropic system. *J. Atmos. Sci.*, (in press).
- _____, D. O'Sullivan, R. Garcia, and P. Callaghan, 1989: Air motions accompanying the development of a planetary wave critical layer. *J. Atmos. Sci.*, (in press).
- _____, R. Garcia, D. O'Sullivan, and P. Callaghan, 1989: The competition between eddy transport and thermal drive in the stratosphere. *J. Atmos. Sci.*, (submitted).
- _____, and R. Garcia, 1989: Dynamical perturbations to the ozone layer: The influence of planetary waves. *Physics Today* (submitted).
- O'Sullivan, D. and M. Salby, 1989: Coupling of the quasi-biennial oscillation and the extratropical circulation in the stratosphere through planetary wave transport. *J. Atmos. Sci.*, (in press).

Research Summary

LARGE-SCALE DYNAMICS AND TRANSPORT IN THE STRATOSPHERE

P.I.: R. Alan Plumb
Massachusetts Institute of Technology

Abstract of Research Objectives

This is a broad-ranging project focussing on dynamics and transport in the southern hemisphere stratosphere and on the dynamics of the mean meridional circulation in the stratosphere. The major current issues being studied are (1) the dynamics of the "final warming" in the southern lower stratosphere and the accompanying transport of ozone-poor air out of the Antarctic vortex into mid-latitudes, (2) the seasonal cycle of planetary waves in the southern stratosphere (unlike the northern hemisphere, there is a minimum of wave activity in mid-winter), and (3) the effects (if any) of the tropospheric Hadley cell on the mean meridional circulation of the stratosphere and the mass flux through the tropical tropopause.

Summary of progress and results

Major progress since this project began on 1 January 1989 is summarized below, separately for the three subtopics noted in the abstract.

(1) Analysis of the southern hemisphere final warming has thus far concentrated on the event of December 1987, a choice which was motivated by the observation that total ozone at Melbourne, Australia (and elsewhere in southern Australia and New Zealand) fell suddenly to record low levels in mid-month, coincident with the "filling-in" of the Antarctic ozone minimum. Potential vorticity evolution (as determined from NMC stratospheric analyses) in the lower stratosphere clearly shows the breakdown of the polar vortex between the isentropic levels 450K and 550K at this time; over a 6-day period in mid-month, potential vorticity increased suddenly in the polar regions and decreased in two bands reaching out to about 30° S, one of which was located across southern Australia and New Zealand and the other across the south Atlantic and southern South America. At and below 450K, there was a corresponding temperature change (implying vertical motion) whose spatial pattern showed a very strong correlation with the potential vorticity changes. This correspondence between horizontal transport and vertical motion is readily explained in terms of classical dynamical "development theory". Over the same period, TOMS data shows changes in total ozone (with decreases exceeding 30DU near 35° S) which also correlates extremely well with these patterns. Using information from ozonesondes at Melbourne and at Lauder, New Zealand, it was estimated that somewhat less than one-half of the ozone decrease observed at Melbourne was associated with the induced ascent (this component of the decrease was therefore

independent of ozone concentrations in the polar vortex) while a little more than one-half resulted from transport of lower ozone concentrations from higher latitudes. Thus it was concluded that the anomalously low total ozone levels over southern Australia and New Zealand in late December 1987 and early January 1988 were probably influenced by ozone depletion in the Antarctic earlier in the spring.

(2) In an earlier study, it was shown that, in a simple "beta-channel" model of forced stratospheric planetary waves, the behavior of the response to a fixed forcing in a seasonally-varying mean flow depends on the forcing amplitude in a way that follows simply from the "Charney-Drazin" condition for wave propagation. For weak forcing, wave propagation into and through the stratosphere is permitted in early and late winter, but not through the summer easterlies nor through the strong westerlies of midwinter. With stronger forcing, the winter westerlies are reduced by the wave transports and in consequence wave propagation occurs through the winter. It was suggested that the southern hemisphere corresponds to the weak forcing case, and the northern hemisphere to strong forcing. However, more sophisticated analysis by Randel of the observed southern stratosphere apparently does not support this interpretation; the "quasigeostrophic refractive index" determined from observational analyses does not show any significant changes through the winter. We have almost completed a study with a linear, hemispheric, quasigeostrophic model, using climatological winds, and find that the observed wave behavior can be reproduced, despite the absence of significant variation in refractive index. The reason appears to be one noted earlier by Simmons in a similar context; in the presence of strong latitudinal curvature in the mean flow, the wave structure changes to mirror the wind structure. Thus, the assumptions of WKB theory (on which the conventional interpretation of refractive index depends) are violated, and, in fact, the "naive" Charney-Drazin criterion proves to be a better indicator of wave propagation than the apparently more sophisticated refractive index, despite the presence of mean wind shear which the former neglects. Apart from application to this issue, these results appear to undermine the value in general of quasigeostrophic refractive index as a diagnostic of wave propagation.

(3) Thus far, investigation has been confined to the question: what is the vertical extent of the steady circulation driven by tropical tropospheric heating? By extending the nonlinear, nearly-inviscid analysis of Held and Hou, it has been shown that the circulation in the inviscid limit does not extend above the levels of heating (and therefore, not above the troposphere). There are reasons to believe, however, that a small amount of viscosity will change this picture; it is planned to test this in numerical experiments.

Journal Publications

Atkinson, R.J., W.A. Matthews, P.A. Newman and R.A. Plumb, "Evidence of the midlatitude impact of Antarctic ozone depletion," *Nature* (27 July), 1989.

- A. CLIMATOLOGICAL STRATOSPHERIC MODELING (673-61-07-30)
- B. DAVID RIND
NASA/GODDARD SPACE FLIGHT CENTER
INSTITUTE FOR SPACE STUDIES (GISS)
- C. TO INVESTIGATE, WITH THE USE OF A 3-D GLOBAL CLIMATE/MIDDLE ATMOSPHERE MODEL, THE IMPACT OF CLIMATE CHANGE ON THE MIDDLE ATMOSPHERE.
- D. During 1988 the GISS 3-D GLOBAL CLIMATE/MIDDLE ATMOSPHERE MODEL was published in two parts. In the first part the model's mean climate for the region between the surface and 85km was discussed based on a 5 year run. The contributions of eddies, the mean circulation and the parameterized gravity wave drag were detailed for both the momentum and thermal fields. Included was a discussion of modeling experiences gained in generating the final version of the model.

In the second part the MODEL VARIABILITY on different time scales was reviewed and compared with observations. It was shown that the model has realistic inter-and intra-seasonal variability, implying that it was not rigidly tuned to produce the mean fields. The role of eddies, the mean circulation, and the gravity wave drag in generating interannual variability was discussed, and it was shown that variations in gravity wave drag, generated by variations in tropospheric processes, were an important component in the modeled variability. The model-generated stratospheric warmings were also presented.

During 1989 the model was used to investigate the EFFECT OF DOUBLED CARBON DIOXIDE ON THE MIDDLE ATMOSPHERE. Carbon dioxide was doubled in both the troposphere and stratosphere, and the sea surface temperatures were increased in accordance with results from the GISS climate model. Additional experiments were run with different sea surface temperature distributions, and doubling the carbon dioxide only in the troposphere or stratosphere.

The results showed that the eddy energy in the middle atmosphere increases in the doubled CO₂ climate, which increases the intensity of the residual circulation. The timing of stratospheric warmings appears to change in response. The potential significance of this change for stratospheric assessments is discussed.

- E. Rind, D., Suozzo, R., Balachandran, N.K., Lacis, A., and Russell, G., 1988: The GISS Global Climate-Middle Atmosphere Model. Part I: Model Structure and Climatology. J. Atmos. Sci., 45, 329-370.

Rind, D., Suozzo, R., and Balachandran, N.K., 1988: The GISS Global Climate-Middle Atmosphere Model. Part II: Model Variability Due to Interactions between Planetary Waves, the Mean Circulation and Gravity Wave Drag. J. Atmos. Sci., 45, 371-386.

Rind, D., Suozzo, R., Balachandran, N.K., and Prather, M., 1989: Climate Change and the Middle Atmosphere. Part I: The Doubled CO₂ Climate. Accepted for publication in J. Atmos. Sci.

General Circulation of the Southern Hemisphere Stratosphere

Principal Investigator: Carlos R. Mechoso
Collaborators: John D. Farrara and Michael Fisher
Institution: Department of Atmospheric Sciences
University of California, Los Angeles
Los Angeles, CA 90024

Research Objectives

The goal of this project is to better understand the dynamical processes at work during the seasonal evolution of the Southern Hemisphere (SH) stratosphere and the reasons for the observed interhemispheric differences in the stratospheric circulation. Our approach to the research is based on two complementary lines of investigation. One uses observational data and aims to provide a three-dimensional picture of the stratospheric circulation. The other uses three-dimensional, primitive-equation numerical models of the atmosphere to test hypotheses arising from the analysis of observational data.

Summary of Progress and Results

The spring circulation in the SH stratosphere evolves in a way that is broadly reproduced year after year. In September, the warm air is over the polar region in the upper stratosphere. Around the strong westerly vortex are transient anticyclones, which develop over the Indian Ocean, travel eastward, and decay over the Pacific Ocean. In October, the westerly vortex becomes highly distorted as a strong, persistent (though fluctuating), planetary-scale anticyclone develops in a preferred geographical location (90°E - 180°). Finally, in November, the vortex breaks down first in the upper stratosphere and then later (and more slowly) in the middle stratosphere. The geographical preference for development of the disturbances is persuasive evidence of a strong connection with zonal asymmetries in surface conditions, particularly with those in orography.

We have illustrated the dramatic changes from winter to spring in the shape of the polar vortex in the stratosphere of the SH using perspective plots of the three-dimensional structure of the isotach and potential vorticity fields. The vortex - an essential meteorological component of the Antarctic 'ozone hole' phenomenon - extends from the upper troposphere. It evolves from a cone, slightly expanding with height and nearly symmetric about the pole, to an inverted cone, distorted and displaced from the pole. The changes in vortex structure from winter to summer are larger in the upper than in the lower stratosphere. In spring, radiative temperature increases are expected to be larger and occur earlier in the upper stratosphere. As a result, the breakdown of the polar vortex is faster and more complete at higher levels.

We have also highlighted the region (generally confined to the lower stratosphere) where temperatures are cold enough for the formation of polar stratospheric clouds (PSCs) - thought to be a key component in the chemical processes leading to ozone destruction. A comparison of lower stratospheric temperatures during winter and spring in the two hemispheres reveals that, in late winter and early spring, conditions suitable for PSC formation are the rule in the SH and the exception in the Northern Hemisphere (NH).

The spring circulation in the NH stratosphere is, in some years, qualitatively similar to that in the SH. For example, the NH final warmings in 1982 and 1985 are similar to SH final warmings in that a persistent anticyclone highly disturbs the westerly circulation. The similarity is closer in 1982, when the breakdown of the westerly circulation proceeds from higher to lower levels, than in 1985, when easterlies develop in the middle stratosphere a few weeks before the westerly circulation in the upper stratosphere turns to easterly. However, during some NH final warmings the flow is much more zonally symmetric and the transition to the summer circulation even more gradual than in the SH.

The build-up in fall of the stratospheric vortex in the northern and southern hemispheres proceed in a broadly similar way - e. g., in both hemispheres the westerly vortex tends to build first in the upper stratosphere - but are notably different in several aspects. The fall stratospheric cooling is comparable in magnitude in the two hemispheres, but the largest temperature changes occur in the upper stratosphere in the NH and in the lower stratosphere in the SH. The seasonal temperature changes have less interannual variability in the SH than in the NH. In the NH, the intensity and position of the jet core can have substantial interannual variations. In the SH, on the other hand, it behaves in a similar way year after year. Sudden warmings are more intense in the NH than in the SH. In both hemispheres, however, one of the major differences between sudden warmings in fall and spring is that the former involve relatively small increases in temperature over the polar region while the latter involve large increases.

We have examined the extent to which the SH stratospheric circulation in early winter is determined by the tropospheric forcing using the U. K. Meteorological Office stratosphere-mesosphere model (SMM) in which fields at the lower boundary, located in the upper troposphere, are prescribed. The SMM is a global, primitive-equation model incorporating an advanced radiation calculation and a parameterization of gravity wave effects. We compare control and anomaly simulations performed with the model for several early winters. Control and anomaly simulations differ in that the initial and boundary conditions are an exact or modified version of the corresponding fields in the observational dataset, respectively. Control simulations are generally very accurate.

Three cases were considered, 1980, 1985 and 1983. In all three cases, zonal wavenumber one (wave 1) in the middle troposphere has large amplitude in early June. In both 1980 and 1985 there is a large upward Eliassen-Palm flux in the upper troposphere and a large, eastward traveling disturbance in the stratosphere. In 1983, on the other hand, the Eliassen-Palm flux in the upper troposphere and the stratospheric disturbances are both weak.

We found that the broad features of the stratospheric disturbances observed during early winter 1980 and 1985 can be simulated by retaining in the initial and boundary conditions only the zonal mean and wave 1. There are, however, important differences between the evolution of the flow in the wave 1-only simulations and that in the control. On the other hand, the simulation is poor if wave 1 at the lower boundary is modified so that its amplitude remains constant in time. These results suggest that the stratospheric and tropospheric circulations during early winter in the SH are strongly coupled.

In the course of our study on planetary-scale disturbances in the SH stratosphere and troposphere during winter we have carried out an empirical orthogonal function (EOF) analysis of winter 500 mb geopotential height anomalies. An earlier EOF analysis using a different dataset pre-filtered the anomalies to exclude wavenumbers five and higher; we do not. The different pre-processing of data affects the results. All three distinct planetary flow regimes identified in the winter circulation of the SH by a pattern correlation method are captured by the new set of EOFs; only two of those regimes were captured by the earlier set. The new results, therefore, lend further support to the idea that EOFs point to distinct planetary flow regimes.

Journal Publications

Mechoso, C. R., A. O'Neill, V. D. Pope and J. D. Farrara, 1988: A study of the 1982 stratospheric final warming in the Southern Hemisphere. *Quart. J. Roy. Meteor. Soc.*, **114**, 1365-1384.

Farrara, J. D., M. Ghil, C. R. Mechoso and K. C. Mo, 1989: EOFs and multiple flow regimes in the southern hemisphere winter. *J. Atmos. Sci.*, in press.

Mechoso, C. R., A. O'Neill, J. D. Farrara, V. D. Pope, M. Fisher and B. Kingston, 1989: On the breakdown of the stratospheric polar vortex in the southern hemisphere. In preparation.

O'Neill, A., V. D. Pope, and C. R. Mechoso, 1989: Final warmings in the Northern Hemisphere stratosphere. In preparation.

Dynamics of Stratospheric Planetary Waves

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Ping Chen, Graduate Research Assistant

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Objectives

We are investigating the dynamics of stratospheric planetary waves using a time dependent linear model. The fundamental question being addressed is: What factors control how much planetary wave activity enters the stratosphere and where it is deposited?

We intend to extend the results of previous linear calculations by including the transience of realistically evolving wave packets. Attention will be focused on: the sensitivity of the distribution of planetary wave driving to modifications of the zonal flow associated with "preconditioning" and the quasi-biennial oscillation; comparisons with a new Rossby wave parameterization scheme developed for use in two-dimensional models by Hitchman and Brasseur (1988); the importance of the zonal flow in the lower stratosphere in determining how much planetary wave activity enters the stratosphere from the troposphere; and the roles of wave-induced changes in the zonal flow and realistic dissipation by radiative transfer and breaking internal gravity waves in determining the distribution of planetary wave driving.

Progress

The time dependent model has been developed and tested. Diagnostic code has been prepared, focusing on the complete budget of Eliassen-Palm wave activity in the model. Numerical experiments, exploring the influence of the mean flow on the time integrated EP flux convergence for wave 1 events, are underway. This work will form the basis for Mr. Ping Chen's PhD dissertation.

In collaboration with Prof. Matthew Hitchman (University of Wisconsin, Madison) we are comparing results from the Hitchman-Brasseur Rossby wave parameterization with the results of a full steady linear calculation. So far these results have been encouraging, and have suggested possible minor modifications of the parameterization.

A. Title: Studies of Large Scale Stratospheric Dynamics Using a Numerical Model Coupled with Observations

B. Investigator: Anne K. Smith
Space Physics Research Laboratory
Department of Atmospheric, Oceanic and Space Science
The University of Michigan

C. Abstract of Research Objectives:

The research addresses questions of the interaction of planetary waves with the mean flow in the stratosphere. Experiments are being run with a global quasi-geostrophic model extending through the middle atmosphere (15-100 km or 0-100 km). Observed zonal mean fields are used in the model to investigate the dependence of wave propagation and wave - mean flow interaction on the basic state for observed cases. Topics that are being or will be studied are 1) the role of preconditioning and/or resonance in observed sudden stratospheric warmings; 2) the effect of stratospheric flow structure on planetary wave propagation in the troposphere; and 3) the impact of tropical and subtropical wind variations on waves in the winter hemisphere. The results are expected to contribute to our understanding of stratospheric dynamics, and will therefore also be important for understanding the transport of trace chemical species in the stratosphere.

D. Summary of Progress and Results

The quasi-geostrophic, time-dependent model used in these studies is fully operational at this time. The model differs from other mechanistic model used for wave-mean flow interaction studies mainly in that it extends to the earth's surface. The zonal mean basic state varies with time due to driving by diabatic heating, interaction with planetary waves and an imposed Rayleigh friction damping. The heating that drives the zonal mean can be either a realistic solar heating, with Newtonian cooling relaxation, or a relaxation back to a prescribed climatological value. In the former case a value of Rayleigh friction that is large in the mesosphere is necessary; in the latter, both the Newtonian cooling and the Rayleigh friction are weak. The realistic heating is needed for long time integrations (more than a few weeks), while a simple relaxation is sufficient for shorter integrations. A geopotential is specified at the top and bottom boundaries or, in the case of a lower boundary at the earth's surface, the residual vertical velocity is set to zero.

A single zonal wave (either wavenumber 1 or 2) is calculated in the model and is allowed to interact with the basic state. The wave geopotential depends on the boundary values and on the (complex) index of refraction squared, which varies strongly with the speed and structure of the basic state zonal wind. Newtonian cooling and Rayleigh friction are included. The wave is forced by a specified lower boundary geopotential perturbation at the tropopause, by a vertical velocity at the earth's surface, or by an internal heat or vorticity source within the troposphere.

The model domain is global, and extends to 100 km. The lower boundary can be located near the tropopause (15 km) or at the earth's surface. The wave and mean geopotential are computed at alternate time steps using an implicit time differencing scheme. The implicit time differencing allows long time steps (12 hours) and makes the model very economical to run.

A number of tests have been run on the model using, as input, observations from the February 1979 sudden stratospheric warming. These indicate that, despite the simplifications inherent in the model, it does a good job of simulating the dynamical evolution of the warming. Tapes of NMC data for the troposphere and stratosphere for other periods have been acquired to use with the model in order to investigate the dynamical processes important during other observed sudden warmings. These other events will be compared and contrasted to the February 1979 case to determine which features are unique to particular events, and which are found in general. These data are now being reviewed to determine the best periods for use in the model simulations.

*A. Title of Research Task:***Upper Atmosphere Dynamics***B. Investigators and Institutions:*

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 Code ES42
 NASA / Marshall Space Flight Center, AL 35812

Dr. Nathaniel D. Reynolds
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C. Research Objectives: The spatial distribution of stratospheric ozone is useful in diagnosis of some features of the large-scale atmospheric circulation, and the ozone may also interact with the atmospheric general circulation. Local maxima in the column ozone distribution are often associated with disturbances in the lower stratosphere and upper troposphere, which may herald cyclone development in the troposphere. One research objective is to explore these issues by means of time series analysis of a zonal index of total column ozone, to suggest the existence or nonexistence of relationships between column ozone and dynamical processes which are known to occur on various time scales. Another objective is to investigate the correlation between the ozone mixing ratio on the 350K isentropic surface and the column integrated ozone, and to investigate the use of an easily derived parameter as a proxy for ozone mixing ratio, which is conserved in the stratosphere for time scales shorter than the photochemical time scale. The source of data for these studies is the Total Ozone Mapping Spectrometer (TOMS) data set furnished by the National Space Science Data Center.

D. 1989 Accomplishments:

1. The zonal index of column ozone z_{O_3} is defined to be the difference between its average in 5-degree-wide bands centered at 60 N and at 30 N. Variations in this zonal index may be due to variations in the meridional transport of ozone in the stratosphere and may also be related to wave activity in the troposphere. A seven-year time series for z_{O_3} has been calculated from the TOMS data for 1981-1987. When the annual cycle is eliminated from the data, there remains evidence of signal from the quasibiennial oscillation, and also from periods of about 30 days, 12-16 days, and 4 to 5 days.
2. Analysis of a time period with a fairly clean wavenumber 1 signature in column ozone is planned. In order to find suitable episodes, video loops of TOMS data for the winters of 85-86, 86-87, and 87-88 have been prepared. The calculation of the pressure of the 350 K isentropic surface is now in progress.

E. Journal Publications: None to date.

A. Title of Research Task: Stratospheric Circulation from Remotely Sensed Temperatures

B. Investigators and Institutions:

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Pasadena, CA. 91109

C. Abstract of Research Objectives:

The objective of the research is to develop an improved quantitative understanding of the large scale circulation of the lower stratosphere in the 15 to 30 km region. Included in the topics addressed are both free and forced waves along with the zonally-averaged component of the circulation. A major theme of the investigation is to examine traditional scaling approximations which have been applied to the stratosphere. Such approximations have been based mainly on tropospheric applications and are not always appropriate for stratospheric problems. When an approximation is found to be inappropriate, an alternative approach is developed. A second theme focuses on the detection and modeling of planetary waves. Both themes involve the use of high quality satellite data which provides both global coverage and good vertical resolution. For these applications, limb observations (Nimbus 7 Limb Infrared Monitor of the Stratosphere {LIMS}) have been found to be superior to other data sets.

D. Summary of Progress and Results:

The past year and a half has seen the development of a powerful spectral analysis tool. Although such techniques are not new, the use of this tool with the LIMS data set represents a significant step forward in our ability to analyse a large amount of high quality data. The tool provides global coverage of power, variance, coherence, and correlations as functions of latitude, longitude, height and frequency for temperature, height, ozone, nitric acid, water vapor, nitrogen dioxide and a wide variety of dynamical quantities which can be derived from these parameters. An immediate benefit has been the identification of both previously documented and newly discovered large scale waves. Many of these features are extremely powerful and represent forces which produce change in the stratosphere. Some of these features appear in the spring in the southern polar regions and are present in both ozone and temperature fields. For example, the variances of temperature and ozone for zonal wavenumber 2 and an eastward period of 8 days are quite large during certain periods.

Simple display of the data does not provide an understanding of the processes which can be identified. Such an understanding can come through the use of models which are closely tied to the data. One such model has been developed to examine linearly unstable waves. Data from the LIMS experiment have been used to define zonally averaged basic state temperature and zonal wind fields in the middle atmosphere for several periods during the winter of 1978-79. This basic state has been used to calculate the phase speeds, growth rates and spatial structures of unstable modes using a linear, quasi-geostrophic model. These results have been compared with temperature and ozone variance amplitudes from the spectral analysis of the same LIMS data. The comparison indicates that there is a close match between phase speeds for the most rapidly growing modes predicted by the model and phase speeds for statistically significant temperature and ozone variances. Both calculated and observed modes tend to be limited in latitudinal extent to a few tens of degrees and in vertical extent to about 10 km. These modes also tend to be non-dispersive. Examples have been found in Southern Hemisphere near mb (30 km).

E. Journal Publications:

- Elson, L. S., 1989: Three-dimensional linear instability modeling of the cloud level Venus atmosphere. *J. Atmos. Sci.*, to appear
- Elson, L. S., 1989: Satellite observations of instability in the middle atmosphere. *J. Atmos. Sci.*, submitted.

IV. DATA ANALYSIS

A. SATELLITE DATA ANALYSIS

B. SUB-ORBITAL DATA ANALYSIS

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A. SATELLITE DATA ANALYSIS

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Title: Analysis of Observations of the Middle Atmosphere from Satellites ..

Investigators and Institutions:

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Co-Investigators: James M. Russell III, William L. Grose, Thomas Miles

All at NASA Langley Research Center

Larry L. Gordley, G & A Technical Software, Inc., 17 Research Drive, Hampton, Virginia 23666

Collaborators: Alan O'Neill and Duncan Fairlie, British Meteorological Office, Bracknell, England

Abstract of Research and Objectives

Satellite data are being used to investigate problems in middle atmosphere chemistry and dynamics. Efforts have been focused primarily on studies to determine the quality of observed distributions of trace species and derived dynamical quantities. Those data have been used as diagnostics for model-derived constituent profiles and fields and for improving our understanding of some of the fundamental processes occurring in the middle atmosphere.

Summary of Progress and Results

Temperatures and derived winds from Nimbus 7 LIMS data have been compared with long-time series of rawinsonde data at Invercargill, New Zealand, and Berlin, West Germany, and the results are excellent for both quantities. It has also been demonstrated that more highly-derived dynamical quantities can be obtained reliably from those LIMS fields. Furthermore, both the diabatic and residual-mean circulations derived using LIMS data agree qualitatively with changes in the distribution of trace species determined independently with the Nimbus 7 SAMS and LIMS experiments. Subsequently, an examination of LIMS data at mid to high latitudes of the Southern Hemisphere has revealed a synoptic-scale, upper stratospheric instability during late autumn that is associated with the development of the stratospheric polar jet. Investigation of this phenomenon continues with Stratospheric Sounding Unit (SSU) data sets.

The LIMS distributions of nitrogen dioxide and water vapor have been reported with a greater degree of certainty, and they provide the basis of a proposed reference atmosphere for those species. The apparent day/night difference in LIMS water vapor has been attributed to non-local thermodynamic equilibrium effects which degrade the daytime LIMS results; the nighttime data are considered more accurate. Extensive studies were performed to determine the quality of several satellite ozone and temperature data sets in the stratosphere as part of the Ozone Trends Study Report. Generally, there was excellent (better than 5 percent) agreement in the mid to upper stratosphere between SBUV, LIMS, and SAGE data of 1978/79. Larger (10 to 20 percent) differences were found in the lower stratosphere; there are uncertainties due to ozone absorption coefficients and to algorithm effects there.

An exploratory study has been conducted to determine seasonal variations in ozone transport in the lower stratosphere using a combination of LIMS ozone profile data plus SBUV total ozone. The technique involves integrating LIMS ozone above the 440K potential temperature surface (just above the tropopause) and then subtracting that amount from a co-located SBUV total ozone measurement. First results indicate excellent agreement at Northern Hemisphere mid latitudes with similar findings from more limited balloon data sets. Whereas the balloon data are concentrated at specific locations in the Northern Hemisphere, the satellite results cover both hemispheres with much more complete spatial coverage each day.

Publications:

Miles, T.; Grose, W. L.; Russell, J. M. III; and Remsberg, E. E.: Comparison of Southern Hemisphere Radiosonde and LIMS Temperatures at 100 mb. QJRMS, 113, 1987, pp. 1382-1386.

Remsberg, E. E.: Analysis of the Mean Meridional Circulation Using Satellite Data. In Transport Processes in the Middle Atmosphere. Edited by G. Visconti and R. Garcia, Reidel, 1987, pp. 401-419.

Remsberg, E. E. and Russell, J. M. III: The Near Global Distributions of Middle Atmospheric H₂O and NO₂ Measured by the Nimbus 7 LIMS Experiment. In Transport Processes in the Middle Atmosphere. Edited by G. Visconti and R. Garcia, Reidel, 1987, pp. 401-419.

Russell, J. M. III: An Interim Reference Model for the Middle Atmosphere Water Vapor Distribution. Adv. Space Res., 7, No. 9, 1987, pp. 5-18.

Russell, J. M. III and McCormick, M. P.: Satellite-Borne Measurements of Middle Atmosphere Composition. Phil. Trans. R. Soc. Lond. A, 323, 1987, pp. 545-565.

Grose, W. L.; T. Miles; K. Labitzke; and E. Pantzke: Comparisons of LIMS Temperature and Geostrophic Winds with Berlin Radiosonde Temperature and Wind Measurements, J. Geophys. Res., 93, pp. 11217-11226, 1988.

Miles, T. and W. L. Grose: Upper Stratosphere Polar Jet Instability in the Southern Hemisphere, Geophys. Res. Lett., 16, pp. 239-242, 1989.

Remsberg, E. E. and C.-Y. Wu: Comparisons of Satellite Ozone Data in the Lower Stratosphere for 1978/79, J. Geophys. Res., 94, pp. 6419-6434, 1989.

An Observational Study of Recent High-Latitude Ozone Variations

Principal Investigator: Kenneth P. Bowman
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Research Objectives

The purpose of the work being conducted under this grant is to diagnose the stratospheric circulation, especially in the southern hemisphere, primarily by using data from the Total Ozone Mapping Spectrometer (TOMS) on Nimbus 7. The work is motivated by two observations. The first is that the seasonal cycles of ozone (and therefore the stratospheric circulations) are very different in the northern and southern hemispheres. Thus we have two different environments in which to test theories of the stratospheric circulation and ozone photochemistry. The TOMS data is extremely valuable for this purpose, because it provides daily, near-global maps of total ozone and is the largest single body of data on southern hemisphere ozone. The second observation is the remarkable downward trend in total ozone detected over Antarctic in the spring season (the ozone hole).

Progress and Results

- 1) Eight years of data from the Total Ozone Mapping Spectrometer (TOMS) on Nimbus 7 were used to estimate globally- and zonally-averaged trends in total ozone over the period 1979 through 1986 (Bowman, 1988). Results were similar to those of the NASA Ozone Trends Panel. The decreases were found to be largest in middle and high latitudes and to occur in all seasons of the year. The decreases were comparable in magnitude to fluctuations observed in the 1960's. Drift in the TOMS instrument calibration introduced considerable uncertainty into the trend estimates.
- 2) Nine years of total ozone measurements from the TOMS were used to study the global structure of the quasi-biennial oscillation (QBO) in total ozone (Bowman, 1989a). Interannual variability of total ozone near the equator (10° S to 10° N) is dominated by the QBO. The equatorial ozone anomalies are independent of season and are well correlated ($r > 0.8$) with the equatorial zonal wind. In both hemispheres, midlatitude anomalies are two to three times larger in winter than in summer. Global patterns of the ozone QBO are identified by computing lagged correlations between the zonal-mean equatorial ozone and ozone elsewhere on the globe. Correlations between equatorial and extratropical ozone are weak during the summer season ($r \sim 0$) and large and negative during the winter ($r < -0.8$ in the southern hemisphere and $r < -0.6$ in the northern hemisphere). There are nodes or phase shifts in the correlation patterns at $\pm 10^{\circ}$ latitude, at 60° S, and at 50° N. Large negative correlations extend to the poles in both winter hemispheres. There are indications of a correlation between wave activity, as measured by the eddy variance of the total ozone field, and the QBO, although the variability of the eddy activity is large and the sample size is small. The correlations support the accepted view that equatorial ozone anomalies result from vertical transport by the QBO circulation. The correlation patterns do not support the theory that extratropical ozone anomalies on the QBO time-scale are the result of either advection of equatorial ozone anomalies by the climatological circulation or quasi-horizontal mixing of the equatorial anomalies by planetary waves. Instead, the ozone anomalies resemble a seasonally-modulated standing oscillation, possibly resulting from quasi-biennial wave forcing of the planetary-scale mean meridional circulation and the associated vertical advection of ozone.

- 3) Nine years of total ozone measurements from the TOMS were used to estimate the meridional transport of ozone during the springtime (September-October-November) breakdown of the Antarctic polar vortex (Bowman, 1989b). Because the vortex breakdown in the Antarctic occurs after the equinox (unlike the Arctic), daily maps of total ozone over the Antarctic region are available for the entire breakdown period. Planetary-scale waves, especially zonal wavenumbers 1 and 2 dominate the eddy variance and ozone transport. Wavenumber 1 is quasi-stationary, while wave number two is eastward moving with a period of ~10 days. During the early spring, vertically-propagating, planetary-scale waves alternately transport ozone poleward and equatorward as their local amplitude increases and decreases. Because the waves propagate through the lower stratosphere, the transport is largely reversible. As the spring season proceeds, the jet weakens and moves poleward and downward in response diabatic processes and forcing by the waves, and the region of wave absorption descends into the middle and lower stratosphere. The interaction between waves and the mean flow then occurs in the lower stratosphere, where non-conservative processes produce irreversible mixing of ozone as the dynamical vortex breaks down. The vortex breakdown and accompanying ozone transport mark the end of the Antarctic ozone hole.

Publications

Bowman, Kenneth P., 1988. Global Trends in Total Ozone, *Science*, **239**, 48-50.

Bowman, Kenneth P., 1989a. Global patterns of the quasi-biennial oscillation in total ozone, *J. Atmos. Sci.*, *in press*.

Bowman, Kenneth P., 1989b. Ozone Transport during the Breakdown of the Antarctic Circumpolar Vortex, *J. Atmos. Sci.*, *submitted*.

Estimating Stratospheric Temperature Trends
Using Satellite Microwave Radiances

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Abstract:

The objective is to evaluate and intercompare stratospheric temperatures using Microwave Sounding Unit (MSU) data as a basis data set. The MSU, aboard the NOAA polar orbiter satellite series, provides twice daily global coverage over a layer (50-150 mb) at approximately a $(170\text{km})^2$ resolution. Conventional data sets (e.g. the NMC, BMO, FUB, radiosondes and rocketsondes) will be compared to the satellite data in the lower stratosphere in order to assess their quality for trend computations.

Summary of Progress and Results:

Approximately 10 years of daily gridded satellite radiance and geopotential height data have been obtained from the British Meteorological Office. This data is comprised of the High resolution Infrared Radiation Sounder (HIRS), the Microwave Sounding Unit (MSU), and the Stratospheric Sounding Unit (SSU). The TOVS instruments provide global coverage of vertical temperature data from the surface to the stratopause. The data was first transferred to magnetic cartridge on the NASA/GSFC IBM 3081 for faster processing. Missing values were linearly interpolated in time at each grid point, such that gaps of eight days or less were filled in. Gaps of nine days or more were left blank. Monthly means of these gridded interpolated data have been computed with a minimum of 20 days of data needed to compute a monthly average. The monthly averaged data have also been transferred from the IBM to the NASA/GSFC PACF VAX for easier temperature trend analysis. Data processing on the IBM required considerable time in learning the system and developing software.

Two other research areas have involved collaborative efforts with colleagues at NCAR, and NASA/GSFC respectively. The first effort involved the comparison of NMC to MSU data, and the comparison of NMC to RAOB data in the Antarctic region. This analysis was performed in order to answer questions concerning temperature trends during the Austral spring. The second research area involved the analysis of lidar observations during October and November 1989 at Table Mountain, California. NMC analyses and RAOB data were used to calculate transport effects on lidar ozone profiles.

Publications:

- Newman, P. A. and W. J. Randel, Coherent Ozone-Dynamical Changes during the Southern Hemisphere Spring, 1979-1986, J. Geophys. Res., 93, 12585-12606, 1988.
- Atkinson, R. J., W. A. Mathews, P. A. Newman, and R. A. Plumb, Evidence of the mid-latitude impact of the Antarctic Ozone Depletion, Nature, 340, 290-294, 1989.
- Nagatani, R. M., A. J. Miller, M. E. Gelman, and P. A. Newman, A Comparison of 1989 AASE Lower Stratospheric Winter Temperatures With Past Data, submitted Geophys. Res. Lett., 1989.
- Mcgee, T., R. Ferrare, J. Butler, P. Newman, D. Whiteman, J. Burris, S. Godin, and I. McDermid, Lidar Observations of Ozone Changes Induced by Air Mass Motions, in preparation, 1989.
- Mcgee, T., R. Ferrare, J. Butler, P. Newman, D. Whiteman, and J. Burris, STROZ LITE: Goddard's Stratospheric Ozone Lidar Trallor, in preparation, 1989.

A STUDY OF THE AEROSOL EFFECT ON UMKEHR OZONE PROFILES USING SAGE II DATA

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ABSTRACT

The study of Aerosol Effects on Umkehr Ozone Profiles using SAGE II Data was proposed for a three-year period. The eight major steps in performing this study are as follows: (1) acquire necessary computer hardware and arrange for off-site mainframe computer time, (2) modify SAGE I computer routines to ingest SAGE II data, (3) construct SAGE II trace constituent files in a standard matrix, accounting for missing events, (4) acquire and ingest Umkehr ozone data during SAGE II period, (5) determine coincident SAGE II/Umkehr cases, (6) create PC-based files and routines to analyze cases, (7) perform statistical analyses to determine aerosol effect on Umkehr profiles, and (8) publish results.

SUMMARY OF PROGRESS AND RESULTS

A significant part of the first-year funding was designated to acquire the computer hardware. The remainder was designated to modify the SAGE I routines and process the SAGE II trace constituent matrices. At this time, we have acquired and installed the computer hardware, modified the SAGE I routines (resulting in approximately 2500 lines of code), processed one quarter of the SAGE II matrices and acquired the Umkehr data. We expect to process the remaining matrices and also to select the coincident cases for study before the end of the first contract year.

The next year of this contract is designated to porting the data to the PC environment and performing the analyses. We have a contractual arrangement and a scientific understanding with Dr. Derek Cunnold at Georgia Tech to analyze the SAGE II/Umkehr cases for aerosol effects. The outline for the scientific analysis is the same as the SAGE I/Umkehr study published in JGR (Newchurch, 1986).

JOURNAL PUBLICATIONS

None

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Newchurch, M.J., "A Comparison of SAGE 1, SBUV, and Umkehr Ozone Profiles Including a Search for Umkehr Aerosol Effects", Journal of Geophysical Research, 92, No. D7, 8382-8390, 1987.

A. Analysis of Stratospheric Ozone, Temperature, and Minor Constituent Data

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C. Research Objectives

The objective of this research is to use available satellite measurements of temperature and constituent concentrations to test the conceptual picture of stratospheric chemistry and transport. This was originally broken down into two sub-goals: first, to use the constituent data to search for critical tests of our understanding of stratospheric chemistry and second, to examine constituent transport processes emphasizing interactions with chemistry on various time scales. A third important goal which has evolved is to use the available SBUV and TOMS data from Nimbus 7 to describe the morphology of recent changes in Antarctic and global ozone with emphasis on searching for constraints to theories. The major effort now being pursued relative to the two original goals is our effort as a theoretical team for the Arctic Airborne Stratospheric Expedition (AASE).

D. Progress and Results

Our effort for the AAOE is based on the 3D transport and chemistry model at Goddard. Our goal is to use this model to place the results from the mission data in a regional and global context. Specifically, we set out to make model runs starting in late December and running through March of 1989, both with and without heterogeneous chemistry. The transport is to be carried out using dynamical fields from a 4D data assimilation model being developed under separate funding from this task. We have successfully carried out a series of single constituent transport experiments. One of the things demonstrated by these runs was the difficulty in obtaining observed low N2O abundances in the vortex without simultaneously obtaining very high ozone values. Because the runs start in late December, this difficulty arises in the attempt to define consistent initial conditions for the 3D model. To accomplish a consistent set of initial conditions we are using the 2D photochemistry-transport model of Jackman and Douglass and mapping in potential temperature, potential vorticity space as developed by Schoeberl and coworkers.

One of the problems in attempting to evaluate the impact of heterogeneous chemistry in three dimensions is that it will not be possible to simply insert all of the relevant reactions. Therefore we undertook a study of how to represent the effects of heterogeneous chemistry in a simplified form. We developed a "ring" model which was one dimensional with longitude as the variable. This model used a specified latitude, altitude and time of year and allowed for advection around the longitude with a polar stratospheric cloud existing over part of the domain. We found that the time scale for heterogeneous processing was rapid, of order 2-3 days. The time scale for recovery was significantly longer. This implies that processing of air trapped in a vortex can be accomplished with minimal cloud occurrences.

Work on TOMS data analysis continued with the observation of the behavior of the Antarctic ozone hole for 1987 and 1988. The 1987 ozone hole was the strongest on record, but 1988 showed a significant recovery. Because of the strong recovery in 1988 of the ozone in the circumpolar maximum region, the declines in ozone in southern midlatitudes do not appear quite as significant as we previously believed. Analyses of global ozone column appear to indicate 3-4% change. North polar changes are generally small, but northern midlatitude winter changes are of the order of 5%

E. Journal Publications in 1988 and 1989

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Jackman, C. H. and P. E. Meade, "Effect of solar proton events in 1978 and 1979 on odd nitrogen abundances in the middle atmosphere", *J. Geophys. Res.* 93, 7084-7090, 1988.

Krueger, A. J., M. R. Schoeberl, and R. S. Stolarski, "The 1987 Antarctic ozone hole: a new record low", *Geophys. Res. Lett.* 15, 1365-1368, 1988.

Krueger, A. J., R. S. Stolarski, and M. R. Schoeberl, "Formation of the 1988 ozone hole", *Geophys. Res. Lett.* 16, 381-384, 1989.

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A Research Summary to
National Aeronautics and Space Administration

Title of Research Task: A Statistical Analysis of Total and Profile Ozone Data for Trend Detection

Principal Investigators: G. C. Reinsel, University of Wisconsin, Madison, and
G. C. Tiao, University of Chicago

Abstract of Research and Objectives

The principal purpose of this research is to perform statistical analyses of worldwide atmospheric total and profile ozone data over the period 1960 to 1987, for the detection of trend. Our research efforts have been concentrated primarily in the following areas: (a) time series analysis of ground-based Dobson total ozone data for trends and solar cycle effects; (b) analysis of total ozone data from the Nimbus-7 SBUV satellite experiment; (c) analysis of revised Dobson total ozone data to investigate ozone trends over different seasons; (d) analysis of the effects of stratospheric aerosols on recent ground-based Umkehr ozone profile measurements and trend analysis of the aerosol-corrected Umkehr data; (e) trend detection capability studies based on variations in the temporal sampling rate and data length of Dobson total ozone and other data.

Summary of Progress and Results

(a) Time Series Trend Analysis of Published Dobson Total Column Ozone Data

Time series regression models which include the 10.7 cm solar flux series as an explanatory variable were employed to obtain trend estimates of total ozone from a network of 37 Dobson ground stations using published data through 1987. Based on the individual station trend estimates, the resulting overall trend estimate for total ozone change over the period 1970–1987, with associated 95% confidence limits, is $(-0.42 \pm 0.58)\%$ per decade. The trends display a rather strong regional variation, with trends in North American stations generally much more negative and trends in India and Japan much less negative. An overall estimate of the effect of 10.7 solar flux on total ozone was obtained as $(0.99 \pm 0.23)\%$ ozone change per 100 units of 10.7 solar flux change, corresponding to about a 1.6 percent change in total ozone from solar cycle minimum to maximum.

(b) Trend Analysis of SBUV Satellite Total Ozone Data

Total ozone data from the Nimbus-7 SBUV satellite experiment were analyzed for the eight year period November 1978 to December 1986. Regression-time series models which include a linear trend term and a 10.7 cm solar flux term were estimated for both monthly average latitudinal zonal averages and a global series. A comparison between SBUV monthly average total ozone data near Dobson ground station locations and the corresponding Dobson station total ozone data for a network of 35 Dobson stations showed an average negative linear drift in SBUV data relative to Dobson data of about -0.4% per year. When the linear trend estimate for the global SBUV series is "corrected" for this negative drift, the 95% confidence interval estimate of the linear trend component in the global SBUV series over this eight year period is $(-0.28 \pm 0.22)\%$ per year. The global estimate of the total ozone-solar flux relation is $(1.05 \pm 0.58)\%$ per 100 solar flux units, which represents a change in ozone over this 8 year period of about $(-1.71 \pm 0.95)\%$ due to solar flux.

(c) Seasonal Trend Analysis of Revised Dobson Total Ozone Data

A trend analysis of Dobson total ozone data that have been critically revised by Dr. Rumen Bojkov has been performed for 27 North Hemisphere stations between 26° N and 64° N latitude using

data through 1986. The trend model considered allows for a different trend for each month of the year to examine the seasonal nature of ozone trend behavior. The trend results indicate significantly more negative trends during the winter months (December-March) than during the summer months (May-August) over the period 1970–1986, with the trends in winter becoming more negative with increasing latitude. The trends in the winter are estimated to be of the order of -1.2% , -2.1% , and -3.0% per decade, respectively, for latitudes 35° N, 45° N, and 55° N, while trends during the summer are of the order of -0.6% per decade with no distinct pattern as a function of latitude. The year-round trend over all latitudes is estimated to be about $-0.84 \pm 0.82\%$ per decade. Trends based on revised data are on average more negative than trends from published Dobson data for European stations, by about -1.0% per decade, with only small average differences for North America and Japan.

(d) Analysis of Recent Umkehr Data for Trends and the Effects of Aerosols

Trend analysis of stratospheric Umkehr profile ozone data from 10 stations over the period 1977–1987 has been considered using two different correction methods to adjust the Umkehr measurements for errors caused by volcanic aerosols. Linear trend models which include the $F_{10.7}$ solar flux term were estimated for each station using both aerosol error correction methods. The trend and solar flux effect estimates are generally similar for both methods. The results indicate a significant overall negative trend, exclusive of trend variations associated with solar flux variations, of the order of -0.5% per year in Umkehr layers 7–9, and a significant positive solar cycle association in all layers 4–9. A comparison between SBUV monthly average profile ozone data near the 10 Umkehr stations and the corresponding Umkehr data corrected for aerosol errors shows a substantial overall negative linear drift in SBUV data relative to corrected Umkehr data in layers 7–9, with estimated values of the drift of the order of -1.0% per year for layers 8 and 9.

(e) Trend Detection Capability Studies

An investigation has been made, based on methodological considerations together with empirical evidence from ozone data, to examine the effects of (i) autocorrelations in the monthly average data and the length of the data records, and (ii) autocorrelations in the daily data and variations in the temporal sampling rate used to form monthly averages, on the precision of trend estimates of stratospheric variables of interest. For factor (i), the impact of the accuracy of the measurements and of the degree of month-to-month autocorrelation in the data on the required data length for trend detection has been determined. For factor (ii), it is shown that when daily measurements are moderately positively autocorrelated, the precision of a trend estimate is little affected whether it is based on monthly averages using all daily values or using only values every other day (or even every fourth day).

Journal Publications

- Bojkov, R., L. Bishop, W. J. Hill, G. C. Reinsel, and G. C. Tiao (1989). A statistical analysis of revised total ozone data over the northern hemisphere, submitted to *J. Geophys. Res.*.
- Reinsel, G. C., G. C. Tiao, S. K. Ahn, M. Pugh, S. Basu, J. J. DeLuisi, C. L. Mateer, A. J. Miller, P. S. Connell, and D. J. Wuebbles (1988). An analysis of the 7-year record of SBUV satellite ozone data: Global profile features and trends in total ozone, *J. Geophys. Res.*, 93, 1689–1703.
- Reinsel, G. C., G. C. Tiao, J. J. DeLuisi, S. Basu, and K. Carriere (1989). Trend analysis of aerosol-corrected Umkehr ozone profile data through 1987, to appear in *J. Geophys. Res.*, 94.
- Tiao, G. C., G. C. Reinsel, D. Xu, J. H. Pedrick, X. Zhu, A. J. Miller, J. J. DeLuisi, C. L. Mateer, and D. J. Wuebbles (1988). Effects of autocorrelations and temporal sampling schemes on estimates of trend and spatial correlation, submitted to *J. Geophys. Res.*.

A. Title: Study of Middle Atmospheric Transports Using Data and Models

B. Investigators and Institutions: John C. Gille, Byron Boville (1988), Guy Brasseur (1988), William Randel (1989) National Center for Atmospheric Research

C. Research Objectives: The objectives of the research are to understand the transports of trace species, chemistry and dynamics in the middle atmosphere by using data from satellites in conjunction with models. The focus is on the study of processes that are incorporated in models, or may serve to test models.

D. Summary of Progress: During 1988 considerable effort went into completing the work, and final writing of Chapter 2, Satellite Instrument Calibration and Stability, for the International Ozone Trends Panel Report: 1988 (Gille, 1988). In this chapter the calibrations of 8 satellite instruments and their stability in orbit were critically evaluated. The major conclusions were that the SBUV and TOMS diffuser plate had degraded in orbit by more than had been previously believed, and that consequently the decrease in ozone in the upper stratosphere was probably considerably smaller than had previously been reported to Congress. Similarly, the decrease in total ozone was probably no larger than suggested by the ground-based Dobson network. On the other hand, the SAGE I and II instruments were found to be stable, and the differences between them small enough that reliable trends over the 5 year differences between their missions could be determined.

In a related task in 1989, a section was prepared for the UNEP Scientific Assessment of Stratospheric Ozone: 1989 (Gille, 1989) This section reviewed the sources of data for present ozone trend analyses, as well as those data anticipated for future analyses. The conclusions were that there is an ongoing integrated ground-based and satellite system for the measurement of total ozone, but that measurements to detect trends in the vertical distribution will require development and improvement of ground-based and satellite systems.

Using newly reprocessed data from the Nimbus 6 PMR, an unexpectedly warm and high stratopause was seen in the Southern Hemisphere winter mesosphere, with an analogous but weaker feature in the Northern Hemisphere. Hitchman et al. (1989) showed that they are not radiatively created, as the lower latitude or summer stratopause is, but are dynamically driven. All evidence points to the deposition of gravity wave momentum as the drive for a downward circulation in the high-latitude winter mesosphere.

Smith et al. (1988) used LIMS data to investigate the eddy transport of non-conserved trace species, often referred to as chemical eddy transport, for ozone, nitric acid, and potential vorticity. An eddy diffusion tensor was calculated for these quantities, based on observed eddy statistics, and compared to transports calculated directly. The chemical eddy terms for ozone explain most of the observed eddy transport in the early winter, but less than half in later winter. The diffusion tensor approach can be implemented in 2D models (as is now occurring). The eddy statistics presented can be used to apply this treatment to any chemically reactive species.

Randel and Williamson (1989) studied the climate of the NCAR Community Climate Model CCM1 in comparison to ECMWF statistics, in particular using wave-mean flow interaction diagnostics to study interrelationships in model biases. Randel (1989a) documented the signatures of baroclinic wave life cycles in the troposphere (and CCM1) using cross correlation analyses; new observations included coherent, wavelike variations in zonal mean wind and temperature tendencies and coherent Ferrel cell vacillations. Randel (1989b) extended these analyses with a comparison to the life cycles of planetary waves

which propagate vertically into the winter stratosphere. Those results may show the first observational evidence of Rossby wave critical layer interactions in the stratosphere. Randel (1989c) documented Kelvin wave-induced oscillations in middle atmospheric tracers measured by LIMS. Cross-spectral analyses with LIMS temperatures demonstrate regions of vertical transport, along with regions of apparent temperature dependant photochemistry. These findings may allow simple testing of middle atmospheric chemical models, and prompt the use of tracer data (such as SBUV) to document Kelvin wave variability.

E. Journal Publications—Published or Submitted Under NASA Order No. W-16, 215, 1988-1989

Brasseur, G., and M. H. Hitchman, 1988: Stratospheric response to trace gas perturbations: Changes in ozone and temperature distributions. *Science*, **240**, 634-637.

Gille, J. C., 1988: Satellite instrument calibration and stability, in International Ozone Trends Panel Report: 1988, WMO Report No. 18, in press.

Gille, J. C., 1989: Observational methods relevant to trend detection, Sec. 2.1 in The Scientific Assessment of Stratospheric Ozone: 1989, R. Watson and D. Albritton, eds., UNEP, in press.

Gille, J. C., 1989: Future observations of the middle atmosphere. In *Proceedings of the NATO Advanced Research Workshop on Dynamics, Transport and Photochemistry in the Middle Atmosphere of the Southern Hemisphere*. A. O'Neill, ed., Dordrecht, Reidel, to appear.

Hitchman, M. H. and G. Brasseur, 1988: Rossby wave activity in a two-dimensional model: Closure for wave driving and meridional eddy diffusivity. *J. Geophys. Res.*, **93**, 9405-9417.

Hitchman, M. H., J. C. Gille, C. D. Rodgers and G. Brasseur, 1989: The separated polar winter stratopause: A gravity wave driven climatological feature. *J. Atmos. Sci.*, **46**, 410-422.

Randel, W. J., 1989a: Coherent wave-zonal mean flow interactions in the troposphere. Accepted *J. Atmos. Sci.*

Randel, W. J., 1989b: A comparison of the dynamic life cycles of tropospheric medium-scale waves and stratosphere planetary waves. In *Proceedings of the NATO Advanced Research Workshop on Dynamics, Transport and Photochemistry in the Middle Atmosphere of the Southern Hemisphere*. A. O'Neill, ed., Dordrecht, Reidel, to appear.

Randel, W. J. and D. L. Williamson, 1989: A comparison of the climate simulated by the NCAR community climate model (CCM1:R15) with ECMWF analyses. Submitted to *J. Climate*, June 1989.

Randel, W. J., 1989c: Kelvin wave induced tracer oscillations in the equatorial stratosphere. Submitted to *J. Geophys. Res.*, August 1989.

Rodgers, C. D., 1989: A comparison of the Curtis-Godson and emissivity growth approximations. Submitted to *Applied Optics*.

Sassi, F., G. Visconti, J. C. Gille and L. V. Lyjak, 1989: Validation of parameterization scheme for eddy diffusion from satellite data. Submitted *J. Atmos. Sci.*

Smith, A. K., L. V. Lyjak and J. C. Gille, 1988: The eddy transport of nonconserved trace species derived from satellite data, *J. Geophys. Res.*, **93**, 11,103-11,122.

Research of Observed and Theoretical Variations of Atmospheric Ozone

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Abstract:

Nine years of Nimbus-7 SBUV ozone mixing ratio (October 1978–September 1987) have been used to analyze the long-term averages of seasonal and longitudinal variations in the lower, middle, and upper stratosphere over latitudes 65°S to 65°N. The annual variation amplitude is maximum over the subpolar regions at about 2 mb, 10 mb, and 40 mb. The semi-annual variation is a maximum at about 4 mb over subpolar latitudes and at about 5 mb over the equator. The effect of the El Chichon aerosol cloud on the annual and semi-annual variation in the tropics is discussed. Analysis of the long-term averaged longitude variation indicates that wave 1 is dominant, particularly during winter, in the Northern Hemisphere.

Research Summary:

A major current problem involving upper atmosphere data analysis is the documentation of the time and space distribution of the principal variables, such as temperature, wind and composition of the stratosphere and mesosphere. During the past two years we have studied the ozone mixing ratio distribution as derived from the Nimbus-7 SBUV observations covering the 9-year period of available data (October 1978–September 1987). Our analyses dealt with the height and latitude distributions of the long-term average annual and semi-annual variations as well as the average major longitude variations. In addition, we documented the hemispheric differences, and in some cases, the year-to-year variations of these distributions. In most cases, the long-term data set was detrended to avoid time changes of the ozone values which were, at least in part, instrument produced.

The average climatological height–latitude ozone distribution confirms the overall patterns derived from earlier limited data coverage. During the winter/summer season, the Southern Hemisphere ozone mixing ratio values over the subpolar regions in the upper stratosphere are considerably higher (~15%)/lower(~5%) than those in the Northern Hemisphere. This is clearly the result of reversed temperature differences between the two hemispheres. In the subpolar middle and lower stratosphere the average ozone mixing ratio is almost always higher in the Northern Hemisphere because of the dominant transport at these levels. Year-to-year variations of the ozone distribution are largest in the subpolar upper stratosphere (1–2 mb) and in the northern subtropics (8–10 mb). The latter is certainly the result of the strong perturbation to the ozone 'observed' distribution caused by the aerosol plume involved in the El Chichon eruption in April 1982.

The effects of the El Chichon eruption on the seasonal ozone variations in the equatorial midstratosphere can be seen in Figs. 1 a,b where we have plotted the monthly mean detrended ozone mixing ratio at 10 mb as derived from the SBUV observations over the 9-year period (dashed lines). Also shown are the computed annual (Fig. 1a) and semi-annual (Fig. 1b) variations. There is an obvious strong reported ozone decrease starting in early 1982 with a slow recovery by 1983. This perturbation extends to at least 10°S.

It has not yet been quantitatively determined as to how much of the ozone 'observed' decrease is an artifact resulting from errors in the data evaluation process associated with the volcanic explosion or is real and is related to ozone photochemical destruction associated with volcanic products.

At 10 mb the annual variation is dominant in the Southern Hemisphere tropical mid-stratosphere. At these latitudes the comparably small semi-annual ozone oscillation arises chiefly from the asymmetry of the annual variation—i.e., faster net ozone decrease than buildup. The amplitude of the annual variation decreases from south to north with a maximum at 20°N. At lower pressures, the amplitude of the semi-annual oscillation is much more symmetric about the equator. It is likely that in the upper layers, the semi-annual variation is, at least in part, a response to the semi-annual solar irradiance maximum in the tropics. At lower elevations (~20 mb) there is a semi-annual ozone maximum likely related to large scale tropospheric convection and subsequent temperature variation both of which are associated with the N-S migration of the thermal equator principally over the Northern Hemisphere tropics.

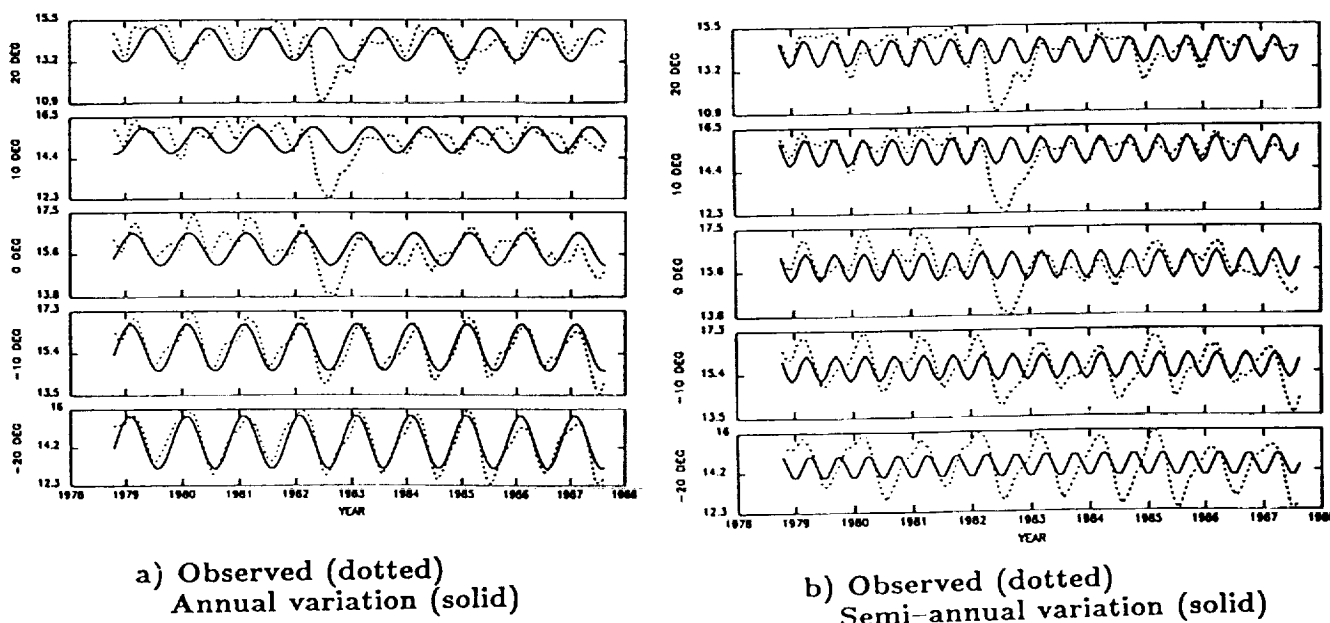
Analysis of the 9-year average longitude variations showed that at all levels the relative amplitude (amplitude/mean mixing ratio) of longitude wave 1 is dominant and is, by far, larger during winter than summer. The winter amplitude maximum is also larger in the Northern than Southern Hemisphere and is farther poleward in the Northern Hemisphere wave. At maximum, the northern winter relative amplitude over subpolar regions at 30 mb is about 10 percent. There is a double maximum of wave 1 over the tropics during all seasons, one at 10 mb, the other at 40 mb with about 150° shift in phase from 10 to 40 mb (from about 20°W to 130°E).

Publications:

London, J. and L. M. Perliski, 1988: Hemispheric differences in observed stratospheric ozone, *Proceeding of the Quadrennial Ozone Symposium*, Göttingen, FRG, August 1988.

Perliski, L. M. and J. London, 1989: Satellite observed long-term averaged seasonal and spatial ozone variations in the stratosphere, *Planetary and Space Science* (special Dobson issue).

Fig. 1. Mid-stratospheric 10mb Ozone Mixing Ratio Variations ($\mu\text{mb}/\text{mb}$) at equatorial and subtropical latitudes (Oct 79 – Sep 87)



Title: Analysis and Interpretation of Variabilities in Ozone and Temperature Fields

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Abstract of Research Objectives:

The purpose of this research is to study the temporal and spatial variabilities of ozone and temperature in the stratosphere on time scales varying from a solar rotation to a solar cycle.

Summary of Progress and Results:

We have studied the temporal and spatial characteristics of short and long term fluctuations in stratospheric ozone and temperature at various pressure levels using several years of ozone , temperature and solar flux data from Nimbus-4, Nimbus-7 and SME satellites. Some of the important results of this study, which have been published in scientific journals and presented at both national and international meetings, are summarized as follows:

a. The solar UV flux and various indices of solar activity indicate a strong period at about 5 months. In the 10.7 cm solar radio flux (F10.7), a conventional index for the solar EUV and UV variabilities, the spectral power of the 5 month period is comparable to the well known 27 day solar period. However, in the solar UV flux at 205 nm, directly measured from the Nimbus-7 SBUV spectrometer, the (spectral) power of the 5 month period is about half that of the 27 day period. In a paper published in the July 1989 issue of the Geophysical Research letters, we have studied the possible impact of the 5 month solar period on ozone and temperature at various pressure levels in the stratosphere and the implications of differences in solar forcing at the 27 day and 5 month periods. It is shown that ozone, both in the lower and the upper stratosphere, has a measurable response to solar UV forcing at 27 days. Such a solar response is not observed at 5 month period because of a relatively weaker 5 month solar UV component in the solar signal and a strong interference from dynamical signals associated with planetary wave activity.

b. Satellite total ozone observations were analyzed using 17 years of data (1970- 1986) from the Nimbus-4 BUV and the Nimbus-7 SBUV experiments. These two data sets show very similar seasonal variations and quasibiennial oscillation(QBO) with some indication of a 4 year component. The QBO maximum and minimum are best correlated with the west and the east components of the QBO wind at 30 mb respectively. For the period 79-86, the ozone standing wave eddies decreased by about 5 percent at 50°N and by about 20 percent at 50°S. These changes are independent of instrument degradation and represent real climatological change

suggesting a decrease in the poleward transport of ozone in the south polar region.

c. The zonal characteristics of both the ozone and temperature trends were derived from ten years (1979-1988) of total ozone and 50 mb temperature based on the Nimbus-7 TOMS measurements and the NMC analyses respectively. The zonal anomalies in ozone and temperature trends are generally in phase and are positively correlated in both the northern and the southern hemispheres. The ozone sensitivity to temperature, derived from their spatial variability, varies from 1-4 percent for 1 K change in temperature and are attributed to dynamical perturbations. After correcting for temperature related changes and instrument drift, the trends in total ozone are still very large (20- 30 percent decrease) in the southern polar region during spring months. It is estimated that about 30 percent of the inferred decrease in total ozone is related to dynamically induced temperature changes and the remaining 70 percent is most probably due to chemistry involving heterogeneous reactions.

Publications:

1. "Satellite Total Ozone Climatology Covering 18 Years", E. Hilsenrath and S.Chandra, Proceedings of International Ozone Symposium 1988, ed. R. D. Bojkov & P. Fabian, A. Deepak Publishing, Hampton, VA.
2. "A Search for a Five Month Solar Induced Periodicity in the Middle Atmosphere", Geophys. Res. Lett., S. Chandra, 16, 711-714, 1989
3. "Response of the Middle Atmosphere to Solar and Dynamical Perturbations, S. Chandra, Middle Atmosphere Program Handbook, In Press, 1989.
4. " Assessments of El Chichon and Solar Cycle Perturbations on Stratospheric Ozone", S. Chandra, Submitted for publication.
5. "The Role of Planetary Waves on Ozone Depletion in the Antarctic," S. Chandra, Submitted for publication.

A. Analysis of Satellite Data to Deduce Stratospheric Constituents and UV Spectroscopic Properties of the Atmosphere

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C. Abstract of Research Objectives

The objective of this research is to better understand the stratosphere, its constituents, and its ultraviolet optical properties, through detailed analysis of data from the SBUV instrument on Nimbus 7 and comparison with data from other instruments, including the NOAA 9 SBUV-2, SAGE, SME, and SMM. One clear conclusion to be drawn from the Ozone Trends Panel report is that there are unresolved differences in the ozone profiles measured by different instruments. While the purpose of the proposed work is more to understand the details of the UV radiation field in the stratosphere than it is to assess the accuracy of the SBUV ozone measurement itself, improved understanding of specific problems in the UV will certainly lead to more accurate ozone retrievals. Areas of study include the effect of aerosols on the backscattered albedo, the shape of the ozone profile near the stratopause, the effect of possible polar mesospheric clouds, and the measurability of nitric oxide and sulfur dioxide.

D. Summary of Progress and Results

A paper was completed this year detailing the results of a study of the long term climatology of nitric oxide based on analysis of gamma band fluorescence features in SBUV continuous spectral scan data. The integrated column amount of nitric oxide above an altitude of approximately 45-50 km is inferred from analysis of the strengths of the (10), (01), and (02) nitric oxide gamma bands. Analysis shows that there are about $5-6 \times 10^{14}$ molecules cm^{-2} of nitric oxide cumulative above 48 km over a wide range of latitudes, increasing sharply near the winter terminator by about a factor of three to $12-15 \times 10^{14}$ molecules cm^{-2} . Between 1979 and 1986 column NO near the equator decreased by about a factor of two, from 6.4×10^{14} molecules cm^{-2} to 3.3×10^{14} molecules cm^{-2} . The time dependence of the decrease correlates well with solar activity, following the decline in solar activity from solar maximum in 1979 to solar minimum in 1985-1986.

In addition work was done to compare measurements made by SBUV with those made by the SBUV-2 instrument on NOAA-9. Because the two satellites are in different orbits, it was necessary to develop a technique to normalize the radiance measurements from each instrument to standard zenith angles so that the measured albedo (radiance to irradiance ratio) could be compared and not just the ozone measurements. This is necessary in order to understand the long term behavior of the calibration of the two instruments, since derived ozone is a very non-linear quantity.

E. Journal Publications

- "Intercomparison of NO Column Measurements during MAP/GLOBUS 1985," McKenzie, R.L., W.A. Matthews, Y. Kondo, R. Zander, Ph. Demoulin, P. Fabian, D.G. Murcray, O. Lado-Bordowsky, C. Camy-Peyret, H.K. Roscoe, J.A. Pyle, and R.D. McPeters, J. Atmos. Chem., 7, 353-367, 1988.
- "The Climatology of Nitric Oxide in the Upper Stratosphere, Mesosphere, and Thermosphere from 1979 through 1986," McPeters, R.D., J. Geophys. Res., 94, 3461-3472, 1989.
- "Long-term Changes in SBUV/TOMS Relative to the World Primary Standard Dobson Instrument," McPeters, R.D. and W.D. Komhyr, in preparation, 1989.
- "Pair Justification: a Technique for Achieving One Percent Accuracy in Satellite Ozone Trend Determination ", R. McPeters, J. Herman, R. Hudson, R. Stolarski, C. Wellemeyer, and S. Taylor, paper presented at the 28th Liege International Astrophysical Colloquium on "Our Changing Atmosphere," Liege, Belgium, 26-30 June, 1989.

The Response of Upper Atmospheric O₃ and NO₂
to Solar UV Variations

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Research Objectives

The project makes use of the data from the instruments on the Solar Mesosphere Explorer (SME) satellite for:

- (1) Analysis of the data on O₃ and solar UV radiation to determine the response of ozone to short-term variabilities in solar UV, and modeling of this response utilizing existing photochemical models of the mesosphere;
- (2) assessing the possibility of utilizing the above data to determine ozone trends in response to solar UV variations during an 11-year solar cycle;
- (3) assessing the possibility of utilizing the NO₂ data from SME to determine response to long-term changes in solar UV.

Progress and Results

We have determined that interference of the El Chichon eruption with NO₂ signal, and drifts in the solar UV and ozone data preclude utilizing the data to investigate (2) and (3). Our work during the second and third years comprised two components: 1) time series analysis of all the available coincident measurements of O₃ and solar UV; 2) modelling the photochemical response of O₃.

The results of our study are as follows:

- There is a high degree of correlation between the changes in Lyman- α and 205 nm radiation measured by the Solar UV spectrometer over the whole 5 years analyzed. However, coincident measurements of O₃ by the UV (UV O₃) and IR (IR O₃) spectrometers do not exhibit the same short-term variability (ie., variations with periods between 5 and 30 days). The lack of correlation between UV O₃ and IR O₃ residuals raises the question of the usefulness of the short-term variations measured by either instrument.
- Analysis of the whole data set yields statistically significant correlations between IR-O₃ and Lyman- α at the altitudes analyzed (50, 60, 68 and 80 km), even after accounting for the decrease in degrees of freedom due to the autocorrelation of the time series. However, the magnitude of the correlation coefficients and time lags at which they peak changes from year to year. The inter-annual changes in the time lag between the IR O₃ and Lyman- α time series cannot be explained in terms of differences in the photochemical response to different spectral components, or as a result of temperature feedback effects induced directly by the solar UV variations.
- The correlation between IR O₃ and Lyman- α is strongest during the summer season for 50, 60 and 68 km. This seasonal behavior would be

expected at 68 km if concentrations of H₂O are larger during the summer than at other times. However, it is unlikely that seasonal changes in water would impact the O₃ below 60 km. The large summer correlation may be due to (coincidentally) stronger signals in the solar UV during this season.

- The calculated response of O₃ to changes in the solar UV between days 90 and 270 of 1982 is weaker than the observed short-term variations in the IR O₃ at 60 and 68 km. A weak positive correlation exists between calculations and data at 80 km; no significant correlation is apparent at 68 km, while calculated and measured ozone are weakly anti-correlated at 60 km. Due to the weak response of the model results to the observed solar UV, calculations over a longer period of time (at least two years) would be required in order to improve the statistics.
- Results from both our data analysis and modelling do not unambiguously identify a photochemical component in the short-term variability observed in the O₃ measured by SME. A major impediment in the identification of such a response is the lack of coincident temperature measurements, which would allow correcting the O₃ data for dynamically-induced variations.
- We have also investigated the possible impact of meteoritic metals deposited in the upper mesosphere on the chemistry of nitric acid in the Antarctic stratosphere during spring. The publication by M. J. Prather and J. M. Rodriguez suggested that formation of stable metal nitrates on aerosol particles could lead to substantial denitrification in the lower stratosphere.

Publications

Prather, M. J. and J. M. Rodriguez (1988) Antarctic ozone: Meteoritic control of HNO₃. Geophys. Res. Lett., 15, 1-4.

Publications in preparation

Rodriguez, J. M., M. K. W. Ko and N. D. Sze. Statistical and modeling studies of the photochemical response of O₃ to solar UV changes over a solar rotation period, as measured by the Solar Mesosphere Explorer (SME).

A. Studies of Middle Atmospheric Radiative and Photochemical Processes using Satellite Data

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C. Research Objectives

(i) Determine the response of middle atmospheric minor species and temperature to short-term solar ultraviolet variations, including latitudinal and seasonal dependences.

(ii) Interpret the derived responses using models of coupled photochemistry and radiative heating. Examine the consistency of the measured responses with model predictions to evaluate the relative contributions of radiative, photochemical, and dynamical processes to the observed responses.

(iii) Apply results of the short-term analysis to better estimate the effect of long-term (11 year cycle) solar UV induced variations on stratospheric ozone and temperature fields.

D. Summary of Progress

(i) Measurements of upper stratospheric ozone and temperature response amplitudes (defined as the percent change for a 1% change in the solar flux at 205 nm) and phase lags were extended to include dependences on latitude (60°N to 40°S) and season (N. H. summer and winter periods). The analysis was based on approximately 4 years of simultaneous Nimbus 7 SBUV ozone and SAMS temperature data. At levels below 3 mbar, ozone response estimates are generally consistent with direct photochemical forcing via changes in photodissociation rates of chemical species, primarily O₂. At levels above 3 mbar the ozone response characteristics are not consistent with direct photochemical and radiative forcing but exhibit dependences on latitude and season that are similar to those of dynamically driven oscillations. The same is true of the temperature responses at all levels. The dynamically driven oscillations are generated as a result of the interaction of upwardly propagating eddies with the zonal mean flow in the winter hemisphere. Therefore, the measurements may provide indirect evidence that solar ultraviolet variations can significantly modulate the upward propagation of planetary waves in the upper stratosphere. Measurements of the response of mesospheric ozone and temperature fields to short-term changes in solar ultraviolet flux are continuing based on analyses of SME IR ozone data and Nimbus 7 SAMS temperature data. In particular, the negative ozone response near 70 km due to photodissociation of water vapor by solar Lyman α variations has been confirmed.

(ii) The derived upper stratospheric responses to solar UV variations have been compared to the predictions of a one-dimensional radiative photochemical model. This work was done in collaboration with A. R. Douglass using an extension of a perturbation-order photochemical model developed earlier by Douglass and R. Stolarski (GSFC). The figure compares the model-calculated ozone response amplitudes and phase lags to low-latitude response measurements derived previously by Hood and Cantrell [1988]. Also shown for

comparison are 27-day response calculations by Brasseur et al. [JGR, v. 92, p. 903, 1987] using a 1-D radiative photochemical code. The current calculated ozone response amplitudes are larger than those estimated by Brasseur et al. because of differences in averaging of the photodissociation rates over solar zenith angle. The calculated amplitudes are within the error bars of the measurements at levels up to about 3 mbar. Above 3 mbar, the data-derived ozone response amplitudes are significantly larger than the model calculations. This is one of several discrepancies that provide evidence for a dynamical component of the coupled ozone and temperature response in the upper stratosphere.

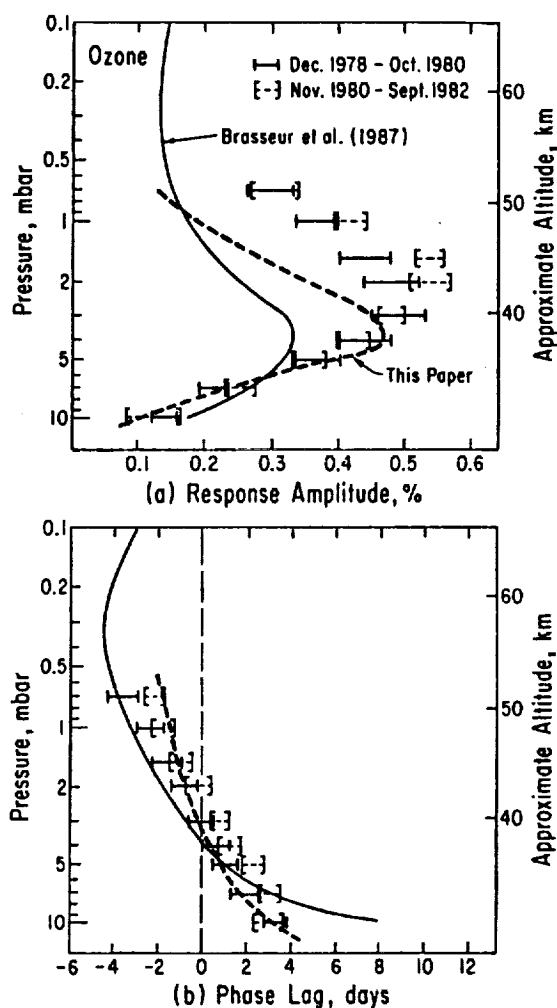
(iii) The same photochemical code used to produce the dashed line model of the figure for the 27-day time scale has been applied in order to calculate the expected long-term variation of ozone mixing ratio at levels between 3 and 10 mbar and at low latitudes during the period of operation of the SBUV instrument. Results show a maximum amplitude of 0.39% at 4.5 mbar (~ 37 km altitude) for every 1% change in the solar 205 nm flux. At other levels, the calculated change is smaller, ranging from 0.34% at 3 mbar to 0.14% at 10 mbar. Adopting a change in the monthly mean 205 nm flux of $\sim 6\%$ between solar maximum in 1980 and solar minimum in 1985 yields a corresponding maximum monthly mean ozone mixing ratio decrease of 2.3% at 4.5 mbar. The net decrease during this interval in total ozone at low latitudes would be less than 1%. However, it is emphasized that this calculation considers only direct photochemical production rate changes; possible solar cycle dynamical effects are not accounted for.

E. Journal Publications

1. Hood, L. L. and Douglass, A. R., Stratospheric responses to solar ultraviolet variations: Comparisons with photochemical theory, *J. Geophys. Res.*, 93, 3905-3911, 1988.

2. Hood, L. L. and Cantrell, S., Stratospheric ozone and temperature responses to short-term solar ultraviolet variations: Reproducibility of low-latitude response measurements, *Ann. Geophys.*, 6, 525-530, 1988.

3. Hood, L. L., Stratospheric responses to solar ultraviolet variations: Dependences on latitude and season, *J. Geophys. Res.*, submitted for publication, 1989.



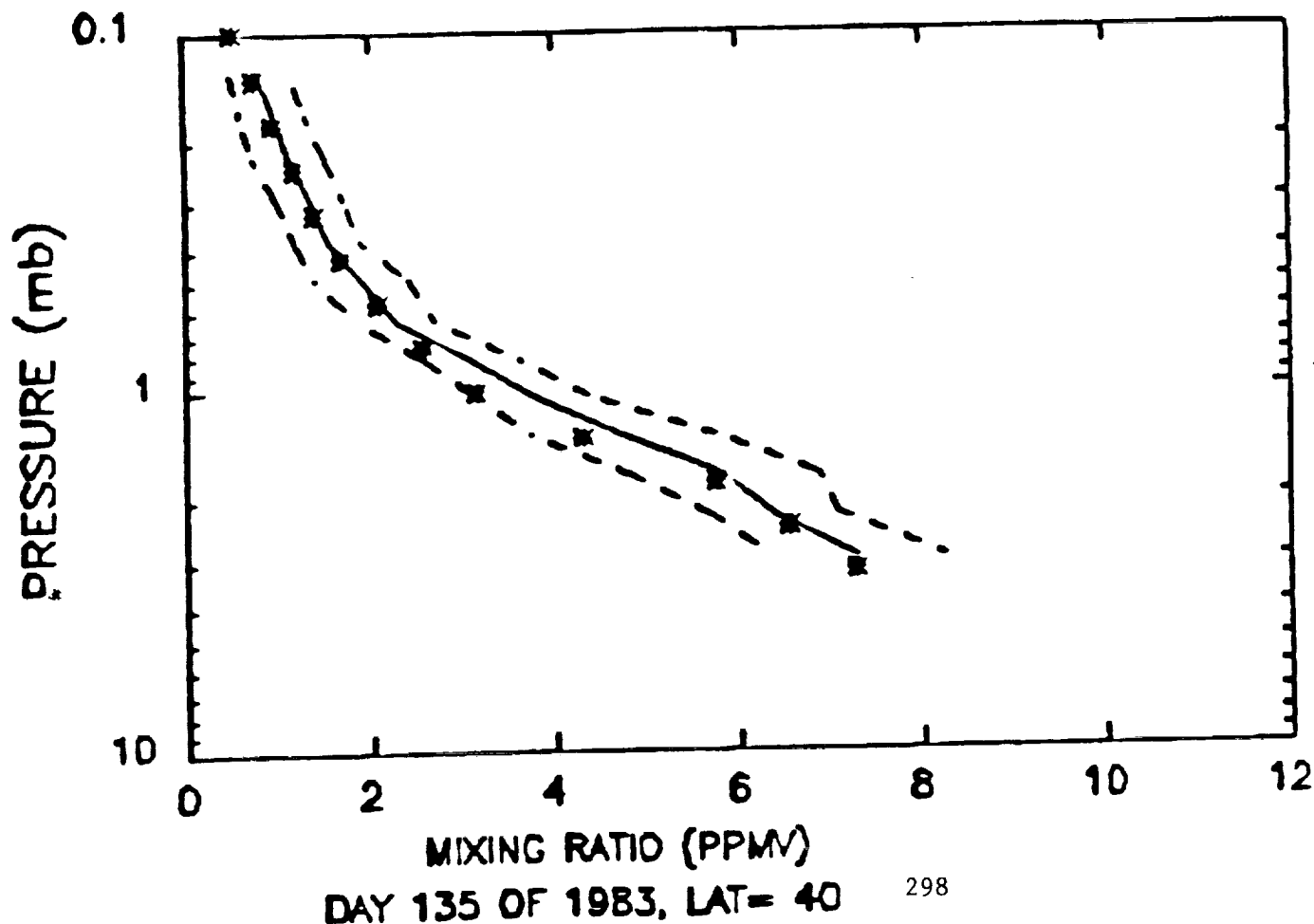
THE REDUCTION AND ANALYSIS OF SME UV DATA

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ABSTRACT

Instruments on the Solar Mesosphere Explorer (SME) have measured ozone in the Earth's atmosphere for five years from 1982 through 1986. These measurements have been analysed and have contributed to our understanding of the chemistry of ozone at and above the stratopause. The Ultraviolet Spectrometer (UVS) on SME has measured atmospheric Rayleigh scattering at a variety of wavelengths during the operation of SME. Ozone densities have been derived only from the wavelengths which provide ozone densities above 1.0 mbar. Additional wavelengths measured will allow the ozone mixing ratios to be determined down to near 40km or about 3 mbar. We are in the process of analyzing these longer wavelength data to obtain ozone densities in the 3.0 to 1.0 mbar region.

In the first 6 months of the grant period, radiance data at the additional four wavelengths have been reduced and placed in the radiance data base. This work is in preparation for the actual inversion to ozone mixing ratios which will begin shortly. This effort will result in an ozone data base which will overlap SBUV and SAGE II measurements and will be compared to these data and to models. A sample inversion of SME UVS data from the six wavelengths is shown in the figure as the asterisks.



THE DETECTION AND INTERPRETATION OF LONG-TERM ATMOSPHERIC
CHANGE: TASKS IN ASSOCIATION WITH THE SHUTTLE SOLAR
BACKSCATTER ULTRAVIOLET RADIOMETER

PRINCIPAL INVESTIGATOR: John E. Frederick
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RESEARCH OBJECTIVES:

This effort is performed in conjunction with the Shuttle Solar Backscatter Ultraviolet (SSBUV) radiometer project at Goddard Space Flight Center. The role of SSBUV is to perform in-orbit calibration updates of operational SBUV/2 ozone monitors carried on NOAA satellites. The objectives of work performed at the University of Chicago are: (a) to define the variables that influence the utility of SSBUV as a calibration standard and (b) to estimate the accuracy with which geophysical trends can be derived from a combined SSBUV-SBUV/2 data set which spans one full decade.

PROGRESS AND RESULTS (1988-89):

We have completed a detailed analysis of the trend detection capability of the SBUV/2 system when SSBUV provides the calibration standard. The quantity to be measured is the ratio of backscattered radiance which emerges from the atmosphere in the vertical to the incoming solar irradiance at 12 wavelengths between 250 and 340 nm. We refer to this as the "backscatter ratio". We have used measured backscatter ratios from the Nimbus 7 SBUV instrument to generate synthetic data bases from SBUV/2 and SSBUV for the time period 1989 through 1999. We impose drifts, presumed to be of instrumental origin, on the SBUV/2 data set, which will be obtained by two to four separate instruments over the decade. In addition we impose a known geophysical trend on the entire data set. The objective is to determine the accuracy with which this geophysical trend can be estimated using SSBUV as a calibration standard.

The SSBUV data set, based on 14 simulated flights over the decade, is then used to remove the drift from each SBUV/2 instrument. The most important factor here is the repeatability of the SSBUV calibration from one Shuttle

flight to the next. When this repeatability is in the range plus or minus 1%, we find that the geophysical trend in backscatter ratio can be recovered to an accuracy of plus or minus 0.9% per decade (two sigma limits).

Reflection from clouds poses a unique problem for the intercomparison of SSBUV and SBUV/2 measurements. The observations to be compared can be separated by as much as one hour, so that changes in cloudiness can hinder attempts to use SSBUV as a calibration standard. We have developed a radiative transfer model that allows a detailed examination of this issue. The results indicate that comparisons between SSBUV and SBUV/2 should not be done at wavelengths longer than 295 nm.

JOURNAL PUBLICATIONS (1988-89):

Frederick, J. E., X. Niu, and E. Hilsenrath, The detection and interpretation of long-term changes in ozone from space, Advances in Space Research 1988, in press, 1989.

Frederick, J. E., X. Niu, and E. Hilsenrath, An approach to the detection of long-term trends in upper stratospheric ozone from space, J. Appl. Meteor., submitted, 1989.

SMM Mesospheric Ozone Measurements

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Research Objectives

The primary objective of this research is to understand the secular and seasonal behavior of ozone in the lower mesosphere, 50 to 70 km. This altitude region is important in understanding the factors which determine ozone behavior. It represents the transition from ozone photochemistry heavily influenced by chlorine compounds and nitrogen oxides to a situation where only hydrogen oxygen reactions are important. Ozone is measured by the technique of solar occultation utilizing the ultraviolet spectrometer polarimeter on the SMM spacecraft. Resulting ozone profiles are used in conjunction with temperature and solar flux data from other experiments to compare predicted ozone variations with observations.

A secondary objective is the investigation of stratospheric ozone in the polar regions. Use is made of results from the SBUV satellite-borne instrument. In the Arctic the interaction between chlorine compounds and low molecular weight hydrocarbons is investigated.

Summary of Progress

More than 30,000 profiles have been obtained using the UVSP instrument on the SMM spacecraft. From mid 1985 through the summer of 1989 several orbits of ozone data per day have been obtained allowing study of the current rise in solar activity from the minimum in mid-1986 until the present. Figure 1 illustrates the observed behavior at sunset within three latitude zones a) $20^{\circ}\text{N} \pm 5^{\circ}$, b) $0^{\circ} \pm 5^{\circ}$, and c) $20^{\circ} \pm 5^{\circ}$. At the equator there is a strong annual minimum in January and semiannual maximum associated with the equinoxes. This pattern is reproduced in an assymetric manner and to a lesser degree at $\pm 20^{\circ}$. There is no secular trend at the equator. At 20°N there is an upward trend in ozone. Both sunrise and sunset profiles are obtained with larger differences between sunrise and sunset with increasing altitude. There is a seasonal behavior associated with these differences.

Analysis of Nimbus 7 SBUV data in Antarctic spring indicates that ozone is depleted within the polar vortex relative to ozone outside the vortex. This depletion confirms the picture of ozone loss at altitudes where polar stratospheric clouds exist. In addition there is ozone loss above the cloud level indicating that there is another mechanism in addition to ozone loss initiated by heterogeneous chlorine reactions on cloud particles.

Publications

Aikin, A. C. and R. D. McPeters, The three-dimensional morphology of the Antarctic ozone minimum, Geophys. Res. Lett., 15, 413-416, 1988.

Aikin, A. C., Ozone minimum occurs in Antarctic in the springtime, Earth in Space, 1, No. 8, 3-5, 1989.

Aikin, A. C., D. Kendig, and H. J. P. Smith, An intercomparison of mesospheric ozone profiles determined by the UVSP and SAGE II solar occultation experiments, Planet. Space Sci., 37, 97-104, 1989.

Aikin, A. C., Mesospheric ozone behavior determined from satellite data, Proceedings of the Biennial Ozone Symposium Gottingen, W. Germany, 1989.

Aikin, A. C., W. Henze, R. Nakatsuku, D. Kendig, and H. J. P. Smith, Variations of mesospheric equatorial ozone as observed by the Solar Maximum Mission, submitted to Geophys. Res. Lett., 1989.

Presentations

Aikin, A. C., D. Kendig, and W. Henze, Mesospheric ozone behavior determined from the ultraviolet spectrometer and polarimeter on the SMM spacecraft, EOS, 69, 1068, 1988.

Kendig, D. and A. C. Aikin, Sunrise/sunset mesospheric ozone differences observed with the ultraviolet spectrometer on SMM, EOS, 70, ,300, 1989.

Aikin, A. C., Nonmethane hydrocarbon influence on the chlorine-induced depletion of Arctic ozone, EOS, 70, 299, 1989.

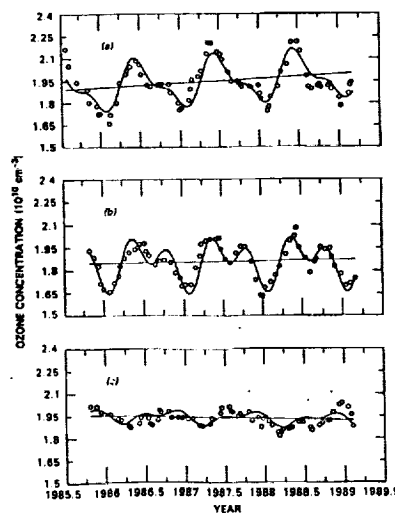


Fig. 1 Sunset ozone concentrations at 55 km measured by the SMM/UVSP instrument (open circles) as a function of time for (a) 20 degrees north, (b) the equator, and (c) 20 degrees south. For clarity of presentation, smoothed weekly means are displayed. Also shown are the fits to the raw data, and the linear trends from the fits.

B. SUB-ORBITAL DATA ANALYSIS

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Global Atmospheric Gases Experiment (GAGE): Overall coordination

Principal Investigator: Ronald G. Prinn, MIT, Cambridge, MA 02139

Objectives: GAGE (nee ALE) comprises continuous in situ high frequency (12 day^{-1}) gas-chromatographic measurements of several chemically and radiatively important species – specifically 2 biogenic/anthropogenic gases (CH_4 and N_2O) and 5 anthropogenic halocarbons ($\text{CFC}\ell_3$, $\text{CF}_2\text{C}\ell_2$, $\text{CH}_3\text{CC}\ell_3$, $\text{CC}\ell_4$, $\text{CF}_2\text{C}\ell\text{CFC}\ell_2$) – at 5 globally-distributed sites (Macehead, Ireland; Cape Meares, Oregon; Ragged Point, Barbados; Point Matatula, American Samoa; Cape Grim, Tasmania). The data are used to determine global trends and lifetimes (or emissions) of each species, to deduce the global average OH concentration, and to deduce global circulation rates.

Summary of 1988-1989 progress:

Ten years of data have now been processed (1978-1988). We have determined that $\text{CC}\ell_4$ has been accumulating in the atmosphere at a rate of $1.3 \pm 0.1\%$ yr over the period 1978-1985 and that the releases of $\text{CC}\ell_4$ into the atmosphere have remained fairly constant, with the smallest release in 1981-1982. Using an inversion scheme based on a nine box model of the atmosphere, we infer a $\text{CC}\ell_4$ lifetime of approximately 40 yr, an inventory on 1 July 1978 of $(2.08 \pm 0.07) \times 10^9 \text{ kg}$ and an average rate of release over the period 1978-1985 of $(9.0 \pm 0.9) \times 10^7 \text{ kg/yr}$. These results produce excellent agreement with a release scenario derived from global production estimates for $\text{CC}\ell_4$ and the major $\text{CC}\ell_4$ byproduct, the chlorofluorocarbons. However, to obtain this consistency, it is necessary that our current ALE/GAGE absolute calibration standard be reduced approximately 25% thus bringing it into agreement with measurements by Yokohata *et al.* (1985) and Hanst *et al.* (1975).

The ALE/GAGE data for nitrous oxide over a ten-year (July 1978-June 1988) time period indicate a global average linear trend in N_2O of $0.30 \pm 0.01\%$ year $^{-1}$ with the increase accelerating at a rate of $0.01 \pm 0.003\%$ year $^{-2}$ in this period. The quoted uncertainties include both 1σ random errors and also systematic errors arising because the measured long-term stability of our calibration standards allows possible biases in the trend and trend acceleration of $0.04 \pm 0.05\%$ year $^{-1}$ (1σ) and $0.004 \pm 0.005\%$ year $^{-2}$ (1σ) respectively. Interpretation of the data using inverse theory and a 9-box (grid) model of the global atmosphere indicates that the measured trends and latitudinal distributions are consistent with the hypothesis that stratospheric photodissociation is the major atmospheric sink for N_2O . However the temporal N_2O increase is not caused predominantly by increases in anthropogenic N_2O emissions associated with fossil fuel combustion, contrary to some previous ideas. Instead, as first noted by Prinn *et al.* (1988), the primary cause for the N_2O trend appears to be a growing tropical source (probably tropical biomass burning and resultant soil disturbance) with fossil fuel combustion playing a secondary (but still significant) role. The new result depends primarily on the ALE/GAGE determination of the N_2O latitudinal gradient rather than the N_2O temporal trend and assumes that the interhemispheric difference in stratospheric N_2O destruction rates is not large. Accepting a theoretically-calculated N_2O lifetime of 166 ± 16 years due to stratospheric destruction only, we deduce from the ALE/GAGE data a 10-year average global N_2O emission rate of $(20.4 \pm 2.4) \times 10^{12} \text{ gm N}_2\text{O year}^{-1}$ but with significant year-to-year variations in emissions associated perhaps with year-to-year variations in tropical wildfires.

Publications

1. Simmonds, P., Cunnold, D., Alyea, F., Cardelino, C., Crawford, A., Prinn, R., Fraser, P., Rasmussen, R., and Rosen, R., 1988. Carbon tetrachloride lifetime and emissions determined from daily global measurements during 1978-1985. *J. Atmos. Chem.*, **7**, 35-58.
2. Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, 1989. Atmospheric trends and emissions of nitrous oxide deduced from ten years of ALE-GAGE data. *J. Geophys. Res.*, submitted.

A. Global Atmospheric Gases Experiment (GAGE)

B. Richard D. Rosen, Ph.D.
Principal Investigator

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C. Abstract of Research Objectives

Continuous gas chromatographic measurements of three biogenic/anthropogenic gases (CH_4 , N_2O and CO) and five anthropogenic gases (CFCl_3 , $\text{CF}_2\text{C}_2\text{Cl}_2$, CH_2CCl_3 , $\text{CF}_2\text{ClCFCl}_2$ and CCl_4) are being made at five sites distributed around the globe. Measurements of five of these species formed the basis for the Atmospheric Lifetime Experiment (*J. Geophys. Res.*, **88**, 8353-8441, 1983), the predecessor of the GAGE program. The GAGE measurements are intended to help document the global distribution and temporal variability of those trace gases that are thought to have potentially important effects on the future evolution of the global climate system. Our role at AER in this multidisciplinary research program is to contribute to the analysis of these data.

D. Summary of Progress and Results

Our participation in GAGE came to a formal end on 14 June 1988, with the termination of contract NASW-4057 on that date. Between 1 January and 14 June 1988, we contributed to the preparation of two scientific papers reporting on the long-term trends in GAGE species. In Simmonds et al. (1988), we analyzed seven years of station data for CCl_4 and, with the aid of a two-dimensional atmospheric transport model, estimated a lifetime for this species of approximately 40 years. In Prinn et al. (1989), we used a ten-year data set to study the trend in N_2O . Among our results is the finding that the linear trend accelerated noticeably during the study period, perhaps because of increased emissions associated with tropical wildfires. We deduce that, in general, the primary cause for the trend in N_2O is tropical biomass burning with fossil fuel combustion playing a secondary, albeit still significant, role. Our analysis indicates that the measured trend in N_2O ($\sim 0.30\%$ year⁻¹) is consistent with the hypothesis that stratospheric photodissociation is the major atmospheric sink for N_2O .

E. Journal Publications, 1988-89

Simmonds, P.G., D.M. Cunnold, F.N. Alyea, C.A. Cardelino, A.J. Crawford, R.G. Prinn, P.J. Fraser, R.A. Rasmussen, and R.D. Rosen, 1988: Carbon Tetrachloride Lifetimes and Emissions Determined From Daily Global Measurements During 1978 - 1985. *J. Atmos. Chem.*, **7**, 35-58.

Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, 1989: Atmospheric Trends and Emissions of Nitrous Oxide Deduced from Ten Years of ALE-GAGE Data. Submitted to *J. Geophys. Res.*

**Data Processing and Analysis Support for the
"Global Atmospheric Gases Experiment (GAGE)"**

Co-Principal Investigators: Fred N. Alyea, Principal Research Scientist
Derek M. Cunnold, Principal Research Scientist

Georgia Institute of Technology, Atlanta, GA 30332

Abstract of Research and Objectives: The GAGE program is a team effort involving several institutions in the United States, Great Britain, and Australia to measure and analyze, at five global sites (Mace Head, Ireland; Cape Meares, Oregon; Ragged Point, Barbados; Point Matatula, American Samoa; Cape Grim, Tasmania), a number of long-lived atmospheric trace gases of importance to man and the environment. The site at Mace Head, Ireland was added to the program in 1987. The gases involved are both biogenic and anthropogenic in origin and include the trace species CFCl_3 , CF_2Cl_2 , CH_3CCl_3 , CCl_4 , N_2O , CH_4 , and $\text{CF}_2\text{ClCFCl}_2$. Measurements are made at each site several times daily using automated gas chromatographs. Each of the participating units has its own particular duties and responsibilities and must accomplish its tasks in concert with the other groups. At Georgia Tech, our primary contribution to the GAGE program includes basic processing and calibration of the raw field data from each GAGE station to dimensional form, preparation and presentation of the resulting data base to the GAGE team for discussion and verification, archival and distribution of the final calibrated and verified record, and analysis of the record in preparation for publication of the GAGE results.

Summary of Progress and Results: Processing of the GAGE raw data from the HP-5880 gas chromatographs located at each of the five global GAGE sites into final calibrated records has essentially been completed through the period ending in December, 1988 and preliminarily through June, 1989. Additional F-113 data from Tasmania is being added to that station's data base backward in time as hand analysis of chromatograms can be prepared in Australia and the results shipped to Georgia Tech. While much of this data was collected prior to the onset of the GAGE program, its existence will add substantially to the GAGE record. It is expected that the Tasmanian F-113 GAGE data will extend from early 1982 onward. In general, the lengths of the data records vary from site to site since the GAGE instruments (HP-5880's) were placed into operation as they became available to each station. Except for the Mace Head site, all of the instruments were on line by mid-1985, however.

During the transition period from the predecessor ALE program (which used HP-5840 chromatographs) to GAGE, maintenance of continuity in the overlapping data base was of great concern. To facilitate this process, at least six months of overlap data was recorded and analyzed at each site. At Tasmania, however, more than 3 years of simultaneous measurements were made and processed. Analyses suitable for comparisons detailing the transition period at each GAGE site have been produced, and the results show clearly that the GAGE data matches in considerable detail the ALE values.

Finally, atmospheric trends and emission of nitrous oxide have been estimated from the ten year record of the ALE/GAGE program. A paper detailing these results has been submitted for publication.

Publications: Prinn, R, D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric Trends in Methyl Chloroform During 1978-1985 and the Global-Average OH Concentration, Science, 238, 945-950, 1988.

Simmonds, P.G., D.M. Cunnold, F.N. Alyea, C.A. Cardelino, A.J. Crawford, R.G. Prinn, P.J. Fraser, R.A. Rasmussen, and R.D. Rosen, Carbon Tetrachloride Lifetimes and Emissions Determined From Daily Global Measurements During 1978-1985, Journal of Atmospheric Chemistry, 7, 35-58, 1988.

Prinn, R. R. Rasmussen, P. Simmonds, D. Cunnold, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric trends and emissions of nitrous oxide deduced from ten years of ALE-GAGE data, Submitted to J. Geophys. Res., August, 1989).

**BIENNIAL RESEARCH SUMMARY
FOR
NASA UPPER ATMOSPHERE RESEARCH AND
TROPOSPHERIC CHEMISTRY BRANCH**

September 1, 1989

A. TITLE OF RESEARCH TASK: Investigation of fine-scale turbulence structure in the upper troposphere and lower stratosphere associated with tropospheric-stratospheric exchange.

B. INVESTIGATORS AND INSTITUTIONS: Dr. Robert L. Grossman, Cooperative Institute for Research in the Environmental Sciences, University of Colorado (Boulder); Dr. Donald H. Lenschow, National Center for Atmospheric Research; Dr. Douglas K. Lilly, University of Oklahoma

C. ABSTRACT OF RESEARCH OBJECTIVES: Describe the fine-scale structure of the atmosphere associated with irreversible turbulent transport of heat, water vapor, and trace gases between the stratosphere and troposphere. Investigate mechanisms which may be involved in irreversible exchange between the stratosphere and troposphere.

D. SUMMARY OF PROGRESS AND RESULTS:

1. Journal article accepted

A climatological study of deep convection over land and ocean during the summer monsoon has been accepted with minor revisions by the Journal of Climate. This work was partially supported by the grant while we were waiting for the Darwin ER-2 STEP data to be properly processed. The study pointed out that the seasonal mean amount of convection in the monsoon region was almost three times the global average. If stratospheric-tropospheric exchange is associated with deep convective clouds, then this study tells where a maximum of exchange is occurring.

2. STEP Turbulence studies

Evidence is increasing that the primary mixing scales associated with breaking waves may be on the order of hundreds of meters. Since our investigation of spectra and cross-spectra indicate that waves are nearly always present in the three missions (we are concentrating on Darwin ER-2 STEP Flights 6,9,12), breaking waves may be an important mechanism for mixing between layers within the transition zone between the stratosphere and troposphere. Unfortunately, on this maiden voyage of the Meteorological Measurement System (MMS) which measured vertical velocity, temperature, and pressure, the sampling rate was only 5s^{-1} (sampling length 40m). As a rule of thumb about 4 equally spaced measurements are necessary to describe a wave so the minimum wavelength which the MMS could have theoretically "observed" was about 160m. However, the analog-to-digital converters appear to have had insufficient resolution at these shorter wavelengths so noise was introduced into the data at sampling lengths below about 200-400 m which may compromise our investigation of small scale turbulence. This can be avoided on future missions by increasing the resolution of the analog-to-digital converters and increasing the sampling rate to at least 20 s^{-1} .

3. Evidence for an upper tropospheric source of NO_y

Despite that negative result, we have some exciting news. In a paper being readied for publication in JGR, Dan Murphy, David Fahey, Shaw Liu, Michael Proffitt, and C.H. Eubank (all of NOAA's Environmental Research Laboratories Aeronomy Laboratory) use synoptic scale

data to argue for an upper tropospheric source of odd nitrogen compounds (NO_y ; total reactive nitrogen). The upper stratospheric source of NO_y is well known and is nearly collocated with the source of ozone. If subjected to the same mixing phenomena, vertical profiles of these two species should be similar (increasing with height) and time series of in situ measurements of O_3 and NO_y from an aircraft moving horizontally through the lower stratosphere or upper troposphere should be highly positively correlated. Furthermore, since O_3 and potential temperature, Θ , are normally highly correlated, NO_y and Θ should be highly positively correlated in time and space. We have found several instances in the STEP data where NO_y and Θ are not well correlated and in some instances exhibit negative correlation. In particular we see periods where Θ is nearly constant while NO_y has a fairly wide range of values (Fig.1).

As you may know we have noted the similarity between the tropopause region of the atmosphere and the thermocline region of the oceans. It is not unlikely that, properly scaled, they may exhibit the same turbulent structure since both are characterized by very high thermodynamic stability. We have been particularly interested in what some oceanographers call "fossil turbulence". Fossil turbulence is the small scale turbulence which occurs after a well-defined active mixing event, such as a breaking wave. Gibson (1988) points out that even though the active mixing events may be very intermittent in time and space, evidence from their occurrence can be found in fossil turbulence which occurs over a longer period of time and diffuses over a larger area. Since the major part of irreversible exchange (highest fluxes) would occur during the active mixing event, the fluxes measured subsequently would be small in comparison. After looking through about six flight hours of ER-2 data, we have observed only one period where relatively high temperature flux was encountered; for the most part fluxes were quite small. Talks with Gibson indicate that our experience is very similar to the analysis of towed thermistor data near the thermocline (i.e., highly turbulent areas are rarely encountered).

After some encouraging discussion with scientists at the NOAA Aeronomy laboratory, we are exploring the following hypothesis. Suppose we are regularly encountering fossil turbulence areas in STEP. Depending upon the time interval between our observation and the active mixing event (perhaps a breaking wave) we would see varying degrees of well-mixed turbulence where Θ was nearly constant in space during nearly level flight (as apposed to flight along an isentrope). After the active mixing event the local field would return to a pre-mixing-event gradient by radiative exchange and by turbulent exchange on a scale much smaller than the active mixing event. The time it takes to accomplish this is typically on the order of 24 hours. If there were no sources or sinks of NO_y and O_3 , then small scale turbulent mixing could reestablish their respective gradients. Little is known about this "relaxation time" but it is probably on the order of 24 hrs or longer. Therefore for some time after a active mixing event Θ , NO_y , and O_3 should show similar characteristics; in this case very small horizontal and vertical gradients (i.e. well-mixed). The anomalous cases we observe where Θ and O_3 appear to have a "well-mixed" signature while NO_y does not can be explained by introducing an upper tropospheric source of NO_y . If a strong NO_y source were near a well-mixed region which contained fossilized turbulence, it would mix the NO_y away from the source diffusing the sharp gradient near the NO_y source into the fossilized region. However, since there is no source for Θ , the Θ field would be unaffected. This would result in scatter plots where Θ varied little while NO_y showed considerable variation. In the case where the NO_y source was below the mixing event, then the gradient of NO_y would be negative (normally it is positive because of the upper stratospheric source of NO_y) and this would cause

occasional areas where there would be a negative correlation between NO_y and Θ as well as between NO_y and O_3 . If we can substantiate this, then we have shown on the meso- to micro-scale what the synoptic and planetary scale work of the NOAA scientists infer: an upper tropospheric source of NO_y .

We should point out that an overturning wave that has not reached a stage where convective (active) mixing is initiated (e.g. breaking) will show negative height gradients of Θ , NO_y , and O_3 . In this case scatter plots would continue to show positive correlation between pairs of variables. We expect this condition to be very rare.

One possible source of NO_y in the upper troposphere is lightning or corona discharge associated with convective activity. This possibility fits our observations from the ER-2 in Darwin, since all of the flights we are investigating so far are over cumulonimbus anvils, a rich source of lightning discharge. We are in touch with scientists involved in lightning research including Dr. John Hallet from Desert Research Institute who was making electric field measurements in EMEX during the time that the ER-2 was deployed to Darwin.

E. JOURNAL PUBLICATIONS:

Grossman, R.L. and O. Garcia, 1990: The distribution of deep convection over ocean and land during the Asian summer monsoon. J. Climate, accepted pending minor revisions.

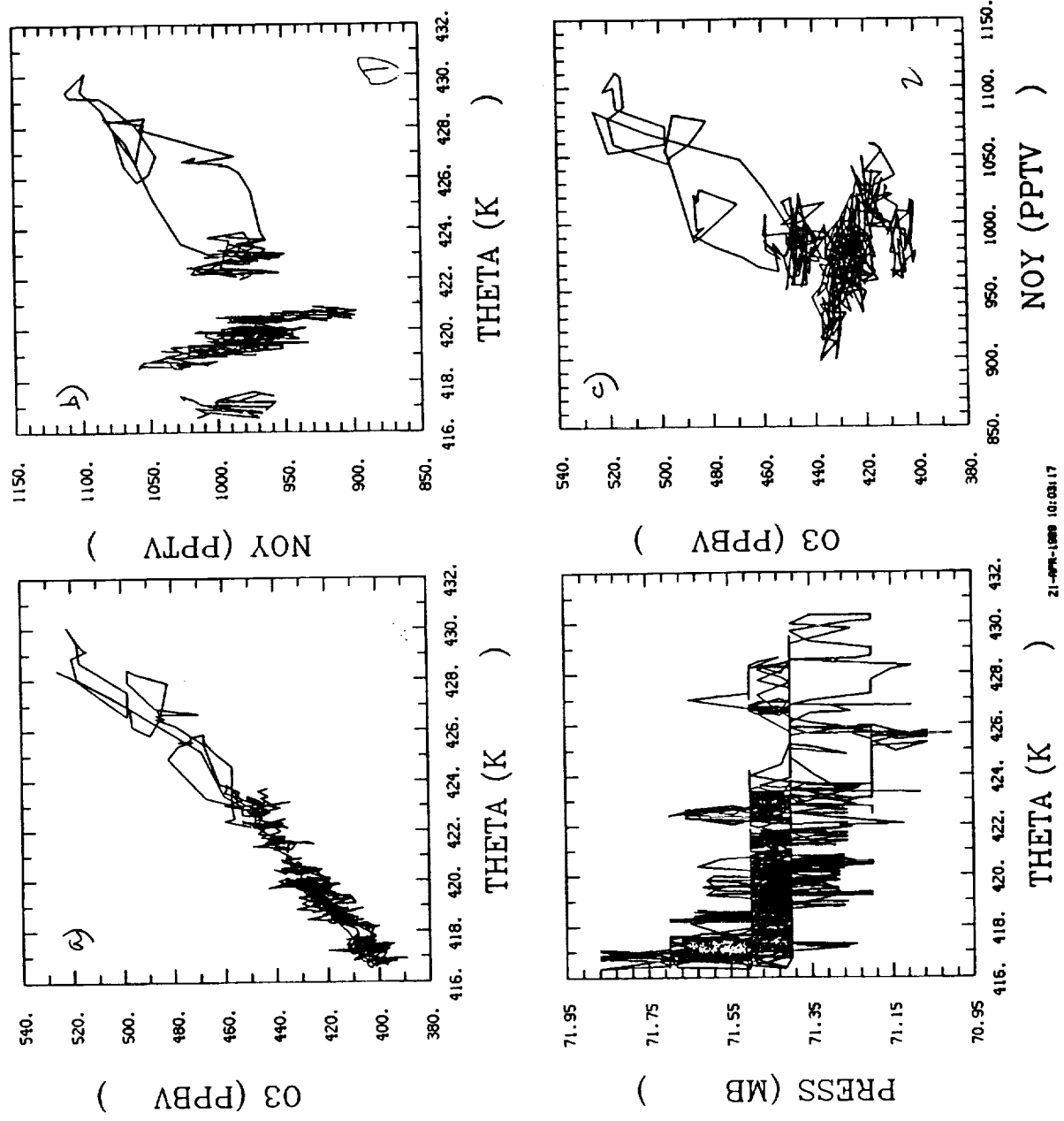


Fig. 1--Scatter plots of a) Θ and O_3 , b) Θ and NO_y , and c) O_3 and NO_y , for a NASA ER-2 flight leg over cirrus clouds associated with active mesoscale convection on 31 Jan 87 during the STEP-Darwin Expedition. Note in b) and c) there is little variation in Θ or O_3 , respectively while NO_y shows considerable variation.

A. Title of Research Task

Data Analysis and Archival

B. Investigators and Institutions

Edwin F. Danielsen (RET), NASA/Ames Research Center
Leonhard Pfister, NASA/Ames Research Center
R. Stephen Hipskind, NASA/Ames Research Center
Steven E. Gaines, Sterling Software

C. Abstract of Research Objectives

The purpose of this task is the acquisition, distribution, archival, and analysis of data collected during and in support of UARP field experiments.

D. Summary of Progress and Results

Meteorological and U2 data from the 1984 Stratosphere-Troposphere Exchange Project (STEP) has been analyzed to determine characteristics of internal atmospheric waves.

CDROMs containing data from the 1987 STEP, 1987 Airborne Antarctic Ozone Experiment (AAOE), and 1989 Airborne Arctic Stratospheric Expedition (AASE) have been produced for archival and distribution of those data sets. The AASE CDROM contains preliminary data and a final release is planned for February 1990.

Comparisons of data from the NASA ER-2 Meteorological Measurement System (MMS) with radar tracking and radiosonde data show good agreement. The results will be published as soon as some recently discovered (small) calibration corrections to the MMS data are made and the data reanalyzed.

Planning for a Meteorological Support Facility continues. We are investigating existing and proposed hardware and software to receive, manipulate, and display satellite imagery and standard meteorological analyses, forecasts, and radiosonde data.

E. Publications

Danielsen, E.F., R.S. Hipskind, and S.E. Gaines, 1989: Irreversible Transport in the Stratosphere by Internal Waves of Short Vertical Wavelength. Accepted for publication in J. Geophys. Res.

Chan, K.R., S.G. Scott, S.W. Bowen, S.E. Gaines, and E.F. Danielsen, 1989: Horizontal Wind Fluctuations in the Stratosphere During Large Scale Cyclogenesis. To be submitted to J. Geophys. Res.

1. Title of Research Task

Analysis of Troposphere-Stratosphere Exchange

2. Investigators and Institutions

Leonhard Pfister, NASA/Ames Research Center, Moffett Field, CA 94035

3. Abstract of Research Objectives

The overall goal of this work is to improve our understanding of stratosphere-troposphere exchange processes in the tropics and midlatitudes. Specifically, we will do modeling and analysis using the aircraft, radiosonde, and satellite data from the 1980 and 1987 NASA tropical field experiments in Panama and Australia, respectively, and the 1986 NASA jet stream field experiment in California. The objectives are to: (1) examine the structure of ozone, temperature, horizontal winds, tropospheric tracers, water and ice particles, and water vapor within, around, and above cumulus anvils in the tropics and jet streams in midlatitudes; (2) establish the presence, during each of the experimental periods, of various potential mechanisms of exchange, such as direct injection by cumulus, gravity wave fluxes, turbulent fluxes, and radiative heating; and (3) evaluate quantitatively, if possible, the mass of air transferred by these mechanisms during specific transport events.

4. Summary of Progress and Results

Our analysis of the 1980 Panama measurements have been devoted to the generation of gravity waves by convection. It is obvious that mesoscale convective systems generate disturbances in the overlying stratosphere. Analysis of the 1980 Panama measurements indicates that these stratospheric disturbances have scales ranging from those of underlying convective plumes (~1 km) to entire anvil systems (~100 km). Using a simple gravity wave model, we have shown that mesoscale convective systems during the experimental period can generate gravity waves in the stratosphere that propagate to stratopause levels, where they break and impart westerly momentum to the flow. Our calculations indicate that they make a significant contribution to the momentum budget of the semiannual wind oscillation.

In addition to continuing our investigation of convectively generated gravity waves using the 1987 Australia data, we have looked into other transport mechanisms with this superior dataset. Our major results to date are: (1) clearly establishing (using wind measurements not available in Panama) that the anvil scale disturbances over convection within the lower stratosphere are gravity waves; (2) documenting an example of shear instability, with subsequent mixing, within an anvil scale gravity wave; (3) establishing that turbulence occurring over a horizontal extent of ~100 km at the top of an anvil can transport tracers

perhaps 1 km or more into the stratosphere; (4) documenting a case of hydration of the lower stratosphere over a convective region by upward mixing of ice particles through the "cold trap" region near the tropopause; (5) discovery of short (5 km length scale) trapped gravity waves in the lower stratosphere, in both convective and clear conditions.

Examination of the 1986 STEP midlatitude dataset has just begun. The most important finding so far is the discovery of a strongly layered structure in the tracers above the midlatitude jet stream, similar to structures found in the 1984 STEP field program. These quasi-isentropic layers are about 1 km thick, and represent undulations of the strong mean gradient of tracers that occurs over the jet stream. There is preliminary evidence (in the form of enhanced small scale variation) that suggests mixing between these layers.

5. Publications

Pfister L., H. B. Selkirk, K. R. Chan, B. Gary, K. Kelly, M. Proffitt, J. Wilson, and R. Knollenberg, 1989: Characteristics of the stratosphere-troposphere interface above a tropical cyclone during STEP Australia. Proceedings of the 18th Conference on Hurricanes and tropical meteorology, American Meteorological Society, San Diego, CA.

Pfister, L., S. Scott, S. Bowen, and M. Legg, 1989: Amplitudes and scales of gravity waves generated by tropical convection. to be submitted to Journal of the Atmospheric Sciences.

A. An Investigation of Mesoscale Variability Using GASP Aircraft Data

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C. Abstract of Research Objectives

The purpose of this research effort was to examine, using the GASP aircraft data set, the geographic variability of mesoscale fluctuations of wind and temperature. Of particular interest was an apparent enhancement, based on a pilot study, of the mesoscale motion spectrum at horizontal scales of 4 to 80 km over mountainous terrain. This suggested that gravity waves excited by high terrain may play a key role in the local forcing of the large-scale atmospheric circulation. It was our intent to extend this analysis to the global GASP data set and to seek evidence of variance enhancements due to other potentially significant sources of mesoscale motions as well. Such information is important in assessing the impact of gravity wave forcing of the lower and middle atmosphere and in determining where observations should be made in order to be most representative of the various wave forcing environments.

D. Summary of Progress and Results

During the first year of this grant, the pilot study conducted with data collected over the continental US and eastern Pacific was extended to the global GASP data set and was stratified further by two measures of terrain roughness. This work showed the same trends as the pilot study (a $\sim 3\times$ enhancement of variance over rough terrain), with high terrain leading to even larger enhancements ($\sim 10\times$). The implications of these results are that high terrain, in particular, plays a disproportionately large role in the excitation of mesoscale (primarily gravity wave) motions and likely thus contributes appreciably to the global energy density and energy flux at these scales. The energy flux by such motions is especially important as it represents, on theoretical grounds, the majority of the energy flux at all scales in the atmospheric fluctuation spectrum. This study is now in press in J. Atmos. Sci.

Additional efforts during 1988 and 1989 have focussed on other potentially important sources of mesoscale activity and geographic variability. Two such sources were judged to warrant additional effort. These are frontal zones, which appear to cause large local enhancements of the velocity and temperature variance at scales less than 64 km, and tropical convection, which causes enhancements over greater areas, but which is less closely coupled with identifiable, discrete sources. In each case, the inferred velocity and temperature variance was computed in 64 km segments along flight paths that crossed zones of convection or frontal activity. The variance estimates were then correlated with evidence of frontal or convective activity obtained from conjunctive satellite imagery. Like the variance enhancements due to high terrain, these sources appear to lead to large, local enhancements of velocity and temperature fluctuations and are likely to represent strong, local forcings of the atmosphere that are highly time dependent. These efforts are continuing and will likely lead to two publications presenting selected case studies and the statistics of variance enhancements due to convection.

Finally, this grant contributed during this period to an assessment of the relative importance and role of gravity waves in forcing the large-scale circulation in the northern and southern hemispheres using evidence collected from a variety of instrument systems. The conclusions of this effort suggest that gravity waves are less prevalent in the southern hemisphere due to the lack of major topography at middle latitudes, but that other sources are necessarily more significant and contribute to lower and middle atmosphere forcing at those locations. This work is in press in a NATO Advanced Studies volume entitled Dynamics, Transport and Photochemistry in the Middle Atmosphere of the Southern Hemisphere.

E. Publications

Jasperson, W.H., G.D. Nastrom, and D.C. Fritts, Further study of terrain effects on the mesoscale spectrum of atmospheric motions, J. Atmos. Sci., in press.

Fritts, D.C., Gravity waves in the middle atmosphere of the southern hemisphere, Dynamics, Transport and Photochemistry in the Middle Atmosphere of the Southern Hemisphere, A. O'Neill and C.R. Mechoso, Eds., in press.

Fritts, D.C., G.D. Nastrom, and W.H. Jasperson, Case studies of mesoscale variance enhancements due to localized gravity wave sources, in preparation.

Nastrom, G.D., and D.C. Fritts, The mesoscale motion spectrum due to frontal and convective excitation, in press.

V. INTERDISCIPLINARY METHANE RESEARCH

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A. Title of Research Task

Biogenic Methane: Fluxes and Isotopic Compositions from Warm Wetland Environments

B. Investigators and Institutions

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C. Abstract

Efforts were directed toward getting good flux and $\delta^{13}\text{C}$ and δD data on atmospheric methane originating from the Everglades and to quantify the flux of methane, resulting from the action of the sun's radiant energy on asphalt and other petroleum products.

D. Summary

Application of stable isotope ratios (δD and $\delta^{13}\text{C}$) to the study of the global CH_4 cycles requires isotopic characterization of the chief atmospheric CH_4 sources. Shallow aquatic sediments are postulated to be an important atmospheric CH_4 source; however, the stable isotope composition of CH_4 produced in these systems is not well defined. Further, the relative importance of the various processes that influence $\text{CH}_4\delta$ values is not generally predictable and probably varies from site to site. We found appreciable seasonal and spatial (probably depth-dependent) variation in the δD and $\delta^{13}\text{C}$ of gas-phase microbial CH_4 produced in the marine sediments of Cape Lookout Bight (CLB), North Carolina. In light of seasonal and depth-dependent variations of CH_4 production from acetate and acetate concentrations in CLB sediments, our observations provide indirect evidence that the CLB $\text{CH}_4\delta$ variation reflects variation in the relative contributions of the main CH_4 precursors (acetate and CO_2/H_2). $\delta\text{D}-\text{CH}_4$ and $\delta^{13}\text{C}-\text{CH}_4$ are inversely correlated, indicating that microbial consumption is not responsible for the δ variation. Owing to its marine nature, CLB is not strictly representative of wetlands in general; however, some of the key microbial processes and environmental characteristics that appear largely responsible for the observed CLB, $\text{CH}_4\delta$ variation are probably similar in typical temperate and high-latitude wetlands.

Estimates of methane flux in the Florida Everglade system ranged over more than 3 orders of magnitude, from about 0.001 to 2.6 g $\text{CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Significant interstation differences in total methane flux were also observed and are judged most likely attributable to differences in the size and spacing of emergent aquatic vegetation, and possibly differences in the type (i.e., vascular plant versus algal) of organic matter incorporated into the sediments. On the basis of measurements presented here and by other investigators, the Everglades system appears to be a relatively weak source of atmospheric methane, probably contributing less than 0.5 Tg $\text{CH}_4 \text{ yr}^{-1}$. Emergent

aquatic plants appear to be capable of indirectly affecting the stable isotopic composition of sedimentary methane by stimulating methane oxidation via root aeration. A significant positive correlation between $\delta D-CH_4$ and $\delta^{13}C-CH_4$ was observed for samples collected from sediments covered by tall, dense stands of emergent plants. In contrast, a significant negative correlation between the δD and $\delta^{13}C$ of sedimentary methane was observed for samples collected at an open water site where ebullition dominated methane transfer to the atmosphere. The mean $\delta^{13}C$ of sedimentary methane samples measured in the Everglades system (mean $\delta^{13}C = -61.7\text{‰}$, s.d. = 3.6‰ , $n = 51$) is not significantly different from the estimated average $\delta^{13}C$ of all natural sources (-58.3‰). The mean δD of Everglades sedimentary methane (mean $\delta D = -293\text{‰}$, s.d. = 14‰ , $n = 50$) appears to be slightly less D-depleted than the estimated average methane ($\delta D = -360 \pm 30\text{‰}$) from all sources.

Diffusion across the air-water interface from several wetland environments in south Florida was estimated from measured surface water concentrations using an empirically derived gas exchange model. The flux from the Everglades sawgrass marsh system varied widely, ranging from 0.18 ± 0.21 mol $CH_4/m^2/yr$ for densely vegetated regions to 2.01 ± 0.88 for sparsely vegetated, calcitic mud areas. Despite brackish salinities, a strong methane flux, 1.87 ± 0.63 mol $CH_4/m^2/yr$, was estimated for an organic-rich mangrove pond near Florida Bay. The diffusive flux accounted for 23, 36, and 13% of the total amount of CH_4 emitted to the atmosphere from these environments, respectively. The average dissolved methane concentrations for an organic-rich forested swamp was the highest of any site at $12.6\mu M$; however, the calculated diffusive flux from this location, 2.57 ± 1.88 mol $CH_4/m^2/yr$, was diminished by an extensive plant canopy that sheltered the air-water interface from the wind. The mean diffusive flux from four freshwater lakes, 0.77 ± 0.73 mol $CH_4/m^2/yr$, demonstrated little temperature dependence. The mean diffusive flux for an urbanized, subtropical estuary was 0.06 ± 0.05 mol $CH_4/m^2/yr$.

E. Journal Publications

- Burke, R.A., Martens, C.S. and Sackett, W.M. 1988. Seasonal variations of D/H and $^{13}C/^{12}C$ ratios of microbial methane in surface sediments of Cape Lookout Bight, USA, *Nature* 332: 829-831.
- Burke, R.A., Barber, T.R. and Sackett, W.M. 1988. Methane flux and stable hydrogen and carbon composition of sedimentary methane from the Florida Everglades, *Global Biogeochem. Cycles* 2: 329-340.
- Barber, T.R., Burke, R.A. and Sackett, W.M. 1988. Diffusive flux of methane from warm wetland environments, *Global Biogeochem. Cycles* 4: 411-425.
- Sackett, W.M. and Barber, T.R. 1988. Fossil carbon sources of atmospheric methane, *Nature* 334: 201.

Research Summary NAGW-835
Analytical Subprogram of NAGW-843

- A. ^{13}C , D, and ^{14}C in Methane
- B. Wallace S. Broecker and Richard D. Fairbanks, Lamont-Doherty Geological Observatory of Columbia University
- C. The primary objective of this program is to derive a quantitative budget of CH_4 from ^{13}C , Deuterium, and ^{14}C . If methane from the various sources can be distinguished and characterized isotopically, then in principle a budget can be obtained from comparison of the isotopic composition of source methane to that of the atmosphere.
- D. Measurements of carbon-14 in small samples of methane from major biogenic sources, from biomass burning, and in "clean air" samples from both the Northern and Southern hemispheres reveal that methane from ruminants contains contemporary carbon, whereas that from wetlands, peat bogs, rice fields, and tundra is somewhat depleted in carbon-14. Atmospheric $^{14}\text{CH}_4$ seems to have increased from 1986 to 1987, and levels at the end of 1987 were 123.3 ± 0.7 percent modern carbon (pMC) in the Northern Hemisphere and 120.0 ± 0.7 pMC in the Southern Hemisphere. Model calculations of source partitioning based on the carbon-14 data, CH_4 concentrations, and $\delta^{13}\text{C}$ in CH_4 indicate that $21 \pm 3\%$ of atmospheric CH_4 was derived from fossil carbon at the end of 1987. The data also indicate that pressurized water reactors are an increasingly important source of $^{14}\text{CH}_4$.
- E. M. Wahlen et al., Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon, *Science*, 245, 286-290, 1989.

A: ^{13}C , D and ^{14}C in methane

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C: The stable isotope composition ($\delta^{13}\text{C}$, δD) and the radionuclide concentration of ^{14}C are investigated in important sources of methane, and are compared to those in atmospheric methane, to more quantitatively assess the strengths of the various sources and their possible variation in time. From stratospheric methane we attempt to determine the isotopic fractionation for ^{13}C and D in the atmospheric destruction reaction with OH. Simultaneous measurements of ^{85}Kr in the atmospheric samples are used to deduce transport parameters for modelling.

D: We continued to add to our data base, and arrived at major conclusions on the global methane budget (see table below).

Measurements of $^{14}\text{CH}_4$ in samples from biogenic sources, biomass burning and in clean air samples from both hemispheres reveal that ruminant CH_4 contains contemporary ^{14}C , whereas that from wetlands, peatbogs, tundra and rice fields is somewhat depleted in ^{14}C . Atmospheric $^{14}\text{CH}_4$ seems to have increased from 1986 to 1988, and at the end of 1987 there was an interhemispheric difference of about 3 pMC. Model calculations based on the $^{14}\text{CH}_4$ data, the CH_4 concentrations and $\delta^{13}\text{CH}_4$ indicate that 21 ± 3 % of the annual 590 Tg CH_4 input to the atmosphere today is derived from fossil carbon. The data also indicate that pressurized water reactors are an increasing source of $^{14}\text{CH}_4$. The biogenic source apportioning is compatible with about 25 % from wetlands, peatbogs and tundra, 19-22% from ruminants, 23-25% from rice production, and 9-10% from biomass burning (for details see ref. E3).

The δD data has been substantially enlarged. δD in atmospheric CH_4 seems to be constant in time, but seems to exhibit a hemispheric difference of about 10 per mil. A correlation is observed between δD in CH_4 emitted from shallow waterlogged environments (wetlands, peatbogs, tundra, rice fields) and δD in local precipitation. This enables the derivation of reliable global values for δD in CH_4 from these sources, as both the global areal extent of inundated land and δD in global precipitation are well characterized.

Isotopic data obtained from stratospheric CH_4 will enable us to determine the fractionation for $^{13}\text{CH}_4$ and CH_3D introduced by the destruction reaction in the atmosphere with OH radical. The results are being interpreted and will yield complementary values to those being obtained in laboratory studies. Preliminary results on the CH_3D fractionation enable us to use the δD data base as an additional independent check on the global CH_4 budget.

Samples	Date	Location (•latitude, •longitude)	CH ₄ (range ppbv) (n= number of samples)	average ¹⁴ C (pMC) (n= number of samples)	average $\delta^{13}\text{C}$ (per mil PDB) (n= number of samples)	average δD (per mil SMOW) (n= number of samples)
North Atlantic	June 1986	50-42 N	8-62 W	1726-1789 (12)	118.6±2.3 (10)	-84±13 (6)
North Atlantic	Febr. 1987	37-44 N	1-60 W	1757-1793 (9)	118.5±1.7 (7)	-88±6 (9)
North Atlantic	Nov. 1987	37-39 N	11-58 W	1747-1792 (6)	123.3±0.8 (5)	-91±4 (5)
Equatorial Atlantic South	Aug./Sept. 1986	5 N-9 S	30-10 W	1657-1676 (5)	115.9±4.5 (5)	-78±4 (6)
Equatorial Atlantic North	Sept. 1986	9-22 N	16-51 W	1680-1784 (3)	117.5±3.9 (2)	-84±10 (2)
North Pacific	July 1986	50-40 N	134-144 W	1696-1766 (6)	117.7±3.2 (6)	-82±4 (6)
Mediterranean and Indian Ocean	Oct./Nov. 1986	7-23 N	37-81 E	1697-1777 (10)	116.9±1.7 (8)	-85±3 (6)
South Pacific	June 1987	10-32 S	90-100 E	1641-1690 (2)	120.0±0.4 (2)	-77±3 (2)
South Pole	Dec. 1987	90 S		1641-1648 (4)	120.0±0.9 (4)	-79±2 (4)
"Clean" land air	1986-1988	9-65 N	44-80 W	1772-1856 (14)	120.4±2.1 (9)	-66.7±0.7 (12)
Contaminated land air	1986-1987	30-59 N	74-96 W	1860-1996 (9)	115.0±2.6 (9)	-66.3±0.5 (8)
	1988	35 S	138 E	2030 (1)	99.1±0.9 (1)	-45.5±0.2 (1)
Stored air samples	1977	42 N	73 W	1722 (1)	103.7±1.4 (1), #113.7±1.5	-46.9±0.2 (1)
	1976	43 N	74 W	1851 (1)	97.4±1.6 (1), #116.2±1.9	-47.3±0.2 (1)
	1978	43 N	74 W	1640 (1)	110.3±1.4 (1), #113.6±1.5	-46.5±0.2 (1)
Methane from oxygen tanks	1966	unknown		20540 (1)	87.6±1.4 (1)	-47.3±0.2 (1)
	1984	unknown		8740 (1)	119.5±1.6 (1)	-45.8±0.2 (1)
Wetland (New York)	1986-1988	43 N	77 W	see table 1	115.8±3.5 (6), #112.7±2.5	-58.3±2.4 (8)
Tundra (Manitoba, Canada)	July 1987	59 N	96 W		113.6±1.7 (6), #112.2±2.0	-62.9±1.9 (8)
Rice (Louisiana)	May/June 1987	30 N	93 W		113.4±2.9 (7), #109.7±9.2	-63.2±2.9 (8)
Peatbog (West Virginia)	May/Nov. 1986	39 N	80 W		117.0±2.2 (4), #116.9±2.4	-56.7±3.3 (8)
Cows	1986-1988				119.8±1.0 (4)	-71.3±4.1 (4)
Termites	Jan. 1987				123.8±1.8 (1)	-68.0±0.2 (1)
Fires	Mar./Aug. 1987				128.3±11.9(3), #137.1±26.4	-26.6±0.4 (2)

All entries for source CH₄, $\delta^{13}\text{C}$ and δD are average values for emitted CH₄, corrected for air content using average clean air values for sampling periods.

corrected assuming excess CH₄ of fossil origin (for details see E3)

* Average values for emitted CH₄, corrected for air content using average values clean air values for sampling periods

- E:
1. M. Wahlen et al., ¹³C, D and ¹⁴C in methane, 13th International Radiocarbon Conference, Dubrovnik, Yugoslavia, June 1988, abstract, p.189-190.
 2. M. Wahlen, Contribution to proceedings of the 1988 Global Change Institute, UCAR, Boulder, CO, August 1988, in press.
 3. M. Wahlen et al., Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon, Science, 245, 286-290, 1989.
 4. M. Wahlen, Contribution to Proceedings of the Dahlem Workshop on Exchange of trace gases between terrestrial ecosystems and the atmosphere, Berlin, FRG, February 1989, in press.

A. The Isotopic Composition of Atmospheric Methane and its Biogenic Sources

B. Paul Quay, Stagg King and Pieter Grootes, University of Washington, Seattle, WA. 98195

C. Research Objectives:

This project has three objectives: the first is to measure the seasonal, latitudinal and interannual trends in the isotopic (i.e. ^{13}C , ^{14}C and D/H) composition of atmospheric methane (CH_4), the second is to use the isotopic composition of CH_4 to quantify the rate and distribution of methane release from abiogenic and biogenic sources and the third is to identify the primary processes that control the isotopic composition of biogenic methane produced during microbial fermentation.

D. Summary of Progress and Results

We have continued our global monitoring of the seasonality of the ^{13}C composition of atmospheric methane (i.e. $^{13}\text{CH}_4$) using biweekly sampling at Pt. Barrow, AK (71°N 156°W), Olympic Peninsula, WA (48°N 126°W) and Mauna Loa, HI (19°N 155°W) and bimonthly sampling at Cape Grim, Australia (41°S 144°E). These measurements started in 1986. We have also continued to measure annual snapshots of the meridional gradients in the ^{13}C and ^{14}C content of CH_4 using shipboard collections of air samples during NOAA oceanographic cruises in the Pacific Ocean. Currently our measurement precision is ± 0.05 ‰ for the $^{13}\text{C}/^{12}\text{C}$ and ± 15 ‰ for the $^{14}\text{C}/^{12}\text{C}$ of atmospheric CH_4 .

Our biweekly $^{13}\text{CH}_4$ measurements have identified several important trends. There is a consistent depletion of up to 2 ‰ in the $^{13}\text{CH}_4$ at high northern latitudes during fall that results from biogenic CH_4 input. There is a fall to summer $^{13}\text{CH}_4$ enrichment of up to 0.7 ‰ at high northern latitudes accompanied by a decrease in CH_4 concentration, which is primarily the result of CH_4 loss by OH oxidation. There is a pole to pole gradient in the $^{13}\text{CH}_4$ of ~ 0.5 ‰, with the most enriched values in the southern hemisphere. Our measurements indicate a global mean $^{13}\text{CH}_4$ of -47.3 ‰ (vs PDB).

We have measured a time series of the ^{14}C content of CH_4 (i.e. $^{14}\text{CH}_4$) since January 1987 at our sampling site on the Olympic Peninsula and have measured annual snapshots of the meridional gradient of $^{14}\text{CH}_4$ using large volume air samples collected during the NOAA cruises. Our $^{14}\text{CH}_4$ measurements indicate a global mean ^{14}C value of ~ 121 percent modern (pM). The $^{14}\text{CH}_4$ is increasing at $\sim 2\text{--}3\%$ per year, based on our measurements at 48°N . Our southern hemisphere samples indicate there is little interhemispheric $^{14}\text{CH}_4$ gradient.

We have incorporated our ^{13}C and ^{14}C measurements into interhemispheric box models and, through a collaboration with Inez Fung (GISS), into a 3-D chemical tracer model. The box model results indicate that our $^{13}\text{CH}_4$ measurements constrain the strength of the CH_4 source derived abiogenically, i.e. from natural gas release and biomass burning, to be $\sim 15 \pm 7\%$ of the total source. Previously, we used the industrial era increase in the $^{13}\text{CH}_4$ to estimate that the abiogenic CH_4 source is $\sim 13 \pm 9\%$ of the total CH_4 source strength (Quay et al., 1988).

Our $^{14}\text{CH}_4$ measurements, incorporated into the box models, constrain the fossil CH_4 source, i.e. natural gas, to be $\sim 12\%$ of the total CH_4 source strength. Although an important component in the global $^{14}\text{CH}_4$ budget is the estimated input of $^{14}\text{CH}_4$ from nuclear reactors which accounts for about $\sim 25\%$ of the global input and is the source of the current $^{14}\text{CH}_4$ increase.

We have measured the ^{13}C composition of CH_4 released from a local bog site over an annual cycle and found that the $\delta^{13}\text{C}$ was relatively constant at approximately -68 ‰ despite a CH_4 flux that varied by a factor of 50. We also measured, using soil

incubations, isotopic fractionation factors of 1.060 to 1.073 for the $^{13}\text{CH}_4$ produced at the local bog site. Our ^{13}C measurements of CO_2 and CH_4 dissolved in soil water and in bubbles collected at wetland sites in Alaska, Minnesota and western Washington yield coexisting alpha values of 1.044, 1.062 and 1.077, respectively. The range in coexisting alpha values suggests that the relative rates of CH_4 production via fermentation and CO_2 reduction pathways varies considerably in wetlands.

E. Journal Publications

Quay, P.D., S.L. King, J.M. Lansdown and D.O. Wilbur (1988). Isotopic composition of methane released from wetlands: Implications for the increase in atmospheric methane. *Global Biogeo. Cycles* 2: 385-397.

Quay, P.D., S.L. King, D.O. Wilbur and S. Wofsy (in press). $^{13}\text{C}/^{12}\text{C}$ of atmospheric CO_2 in the Amazon basin: forest and river sources. *J. Geophys. Res.*

King, S.L., P.D. Quay and J.M. Lansdown (accepted). $^{13}\text{C}/^{12}\text{C}$ kinetic isotope effect for soil oxidation of methane at ambient atmospheric concentrations. *J. Geophys. Res.*

A. Title of Research Task

Seasonal $\delta^{13}\text{C}$ Variations of Biogenic Methane: Biogeochemical Controls

B. Investigators and Institutions

Neal Blair, Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695

C. Abstract

Isotopic measurements of methane can be used to determine the sources of that gas to the troposphere and to evaluate global budgets. It is well established that the flux and isotopic composition of methane varies seasonally in temperate environments thus complicating the use of isotopic measurements. The primary objectives of this project have been to determine the mechanism of the seasonal variations and to develop a quantitative model that describes the variations. It has been hypothesized that the seasonal variations result from changes in the relative rates of the two methanogenic pathways, CO_2 reduction and acetate dissimilation. Carbon isotope measurements of the methanogenic precursors, dissolved inorganic carbon (DIC) and acetate were made on material isolated from methane-producing sediments to test that hypothesis.

D. Summary of Progress and Results

A diagenetic model has been completed which successfully predicts the seasonal and annual methane fluxes from the organic-rich sediments of Cape Lookout Bight, NC using relatively simple geochemical measurements (DIC, sulfate). Future work involves extending the model to other environments and to the prediction of the isotopic signature of methane from those environments. Initial efforts to use a mass balance model in a salt marsh have been successful in verifying the flux and isotopic composition of methane leaving the site. In collaboration with J.P. Chanton (Florida State University), we have discovered that the diffusion of methane through the salt marsh plants results in a carbon isotopic fractionation of approximately 19 per mil. Thus, methane leaving the marsh is significantly depleted in ^{13}C relative to that in the marsh sediments.

Inter- and intramolecular carbon isotope measurements have been made on acetate isolated from marine and freshwater sediments. The isotopic composition of acetate can be explained in terms of the $^{13}\text{C}/^{12}\text{C}$ ratio of the metabolizable organic carbon fraction and the isotopic discrimination that occurs during the dissimilation to methane and CO_2 . Because acetate dissimilation is responsible for up to 70% of methane production in freshwater environments, the information concerning isotopic fractionations during acetate cycling is critical for models that describe the controls of the $^{13}\text{C}/^{12}\text{C}$ ratio of methane.

The importance of the DIC measurements to our models has led us to design and build a portable unit for the measurements. The instrument, which measures DIC concentration and prepares the sample for isotopic measurements, is currently being field-tested.

The accuracy and precision of isotopic analyses are often limited by sample size. A small sample inlet system has been constructed for our group's mass spectrometer which should allow the measurement of samples with sizes down to 10 nmoles. The extended range of the measurements will make new types of atmospheric studies feasible. The inlet system is scheduled to be fully operational by the end of 1989.

E. Journal Publications

Seasonal Variations in the Production of ΣCO_2 in a Methane-Producing Marine Sediment: in preparation (S.E. Boehme, N.E. Blair, J.P. Chanton).

Carbon Isotope Biogeochemistry of Acetate Cycling in an Anoxic Marine Sediment: in preparation (N.E. Blair and W.D. Carter).

RESEARCH SUMMARY: NASA GRANT NAGW - 834

- A. Seasonal Variations in Isotopic Signatures of Methane Produced in Organic-Rich Environments
- B. Christopher S. Martens, Jeffrey P. Chanton and Larry K. Benninger, University of North Carolina, Chapel Hill; Neal E. Blair, North Carolina State University, Raleigh.
- C. The specific objectives of our NASA project were to:
 - i) investigate seasonal variations in the isotopic signatures of methane from a range of organic-rich environments including coastal and estuarine sediments and wetland soils,
 - and ii) seek relationships between methane production rates and fluxes, isotopic values and organic carbon degradation in sedimentary environments.

We also have begun to collect samples for and have made preliminary arrangements to utilize newly developed accelerator mass spectrometry for methane radiocarbon measurements. It should also be noted that the work has been carried out in conjunction with a previously funded NASA project focusing on the use of radon-222/radium-226 disequilibrium to trace physical processes controlling biogenic gas fluxes to the troposphere.

- D. Summary of Progress (1988-89): Progress on the first objective includes documentation of variations in carbon stable isotopic composition of methane from river-estuarine systems, wetlands, Amazon capims (floating grass mats), and Alaskan tundra environments (see publications list). Almost all of our isotope measurements from 1988-89 were made on our new Finnigan MAT-Delta E stable isotope mass spectrometer facility dedicated to this project. This instrument is shared with Dr. Neal Blair of N.C. State University.

The evolution of the NASA ABLE-3a mission to include studies of gas fluxes from tundra wetland and tundra lakes near Bethel, Alaska, presented a unique opportunity for a high latitude field study in conjunction with aircraft overflights and micrometeorological tower facilities. Our purpose in conjunction with this project was to characterize the carbon isotope composition of methane produced and being transported to the atmosphere from tundra environments. As it turned out we were able to hire an employee of the U.S. Fish and Wildlife Laboratory in Bethel to continue our lake sampling until lake freeze-up in October. We thus had an opportunity to look for "seasonal variations" in methane isotopic composition using data from early July through mid-October. We were able to collect an unexpectedly large

number and variety of gas samples in Alaska as a result of unprecedented good weather and some good fortune in locating suitable field sites around Bethel as well as cooperation from people manning the Lake ABLE tower site. We have already run over 90 methane isotope samples from various tundra sites.

We have made significant progress in setting up to carry out combined carbon and hydrogen isotopic work on samples from the sites mentioned above. We expect to be able to study hydrogen isotopic composition of Alaskan tundra methane using existing samples plus new ones to be collected during 1989-90. We also expect to make our first accelerator radiocarbon measurements this fall on methane samples from Alaskan tundra lakes.

E. Journal Publication Supported by NAGW-834 (1988-89):

Chanton, J.P. and C.S. Martens. 1988. Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. Global Biogeochem. Cycles 2: 289-298.

Chanton, J.P., G.G. Pauly, C.S. Martens, N.E. Blair and J.W.H. Dacey. 1988. Carbon isotopic composition of methane in Florida Everglades soils and fractionation during its transport to the troposphere. Global Biogeochem. Cycles 2: 245-252.

Burke, R.A., C.S. Martens and W.M. Sackett. 1988. Seasonal variations of D/H and $^{13}\text{C}/^{12}\text{C}$ ratios of microbial methane in surface sediments. Nature 332: 829-831.

Chanton, J.P., P.M. Crill, K.B. Bartlett and C.S. Martens. 1989. Amazon capims (floating grassmats): A source of ^{13}C enriched methane to the troposphere. Geophys. Res. Lett. 16: 799-802.

Martens, C.S., J.P. Chanton, C.A. Kelley, J.K. Cox and W.B. Showers. 1989. Carbon and hydrogen isotopic signature of methane emitted from Alaska's Yukon-Kuskokwim Delta. (Manuscript in preparation; abstract published: Trans. Amer. Geophys. Union 70:

Kelley, C.A., C.S. Martens and J.P. Chanton. 1989. Variations in sedimentary carbon remineralization rates in the White Oak River Estuary, North Carolina. Limnol. Oceanogr. (in press).

Not listed are four additional published abstracts from the November, 1988 and April, 1989 AGU meetings. C.S. Martens presided over the Global Tropospheric Chemistry III session at the April, 1989 meeting.

***Investigation of the Trends in the Isotopic Composition of Atmospheric Methane -
NASA Grant W16188***

C. M. Stevens, Chemistry Division, Argonne National Laboratory
H. Craig, Scripps Institute of Oceanography, University of California at San Diego
R. A. Rasmussen, Department of Environmental Science, Oregon Graduate Center

Research Objective

The objective of this program was to measure the temporal trend of the stable carbon isotopic composition of atmospheric methane, both for the past decade and for past centuries. These results would provide constraints for determining the relative contributions to the increasing concentration of atmospheric methane from the changing fluxes of the isotopically different anthropogenic and natural sources.

Summary of Progress and Results

The sources of atmospheric methane consist of a number of different generic natural and anthropogenic origins, whose $^{13}\text{C}/^{12}\text{C}$ isotopic ratios are for the most part characteristic of the origin and vary over a wide range of four percent. The most abundant sources are the natural wetlands, rice paddies, and herbivores which produce methane by anerobic fermentation processes highly depleted in carbon-13, while burning biomass and the anthropogenic activities associated with natural gas systems and coal mining produce methane enriched in carbon-13. The isotopic composition of atmospheric methane provides a constraint on the relative distribution of the fluxes of these isotopically different sources; likewise the temporal trend of the isotopic composition constrains the relative magnitudes of any changing fluxes of these sources. The unequal distribution of the anthropogenic sources in the hemispheres along with limited mixing by interhemispheric exchange provides another constraint in establishing the causes of different isotopic trends between hemispheres. Figure 1 shows the results of isotopic measurements for both hemispheres from 1978 to 1989.

The $^{13}\text{C}/^{12}\text{C}$ ratio has been increasing in both hemispheres, with a greater rate in the southern hemisphere. The average trend over the decade in the average isotopic ratios of the source fluxes in each hemisphere are calculated as +0.5 per mil/yr for the southern hemisphere and -0.07 per mil/yr for the northern hemisphere. This calculation is based on 0.8/yr for the interhemispheric exchange rate and 8 years for the lifetime of atmospheric methane. The southern hemisphere trend was most certainly caused by increasing fluxes calculated at 3-4 Tg/yr² of isotopically heavy CH_4 (enriched in ^{13}C) from the rapidly increasing activity of biomass burning, the only significant anthropogenic source in this hemisphere. In the northern hemisphere the trend of the $^{13}\text{C}/^{12}\text{C}$ ratio of the sources, calculated from independent estimates of the growth rates of the anthropogenic sources, should be in the range +0.1 to 0.2 per mil/yr, in wide disagreement with the measured negative trend. Based on this disparity it is deduced that the fluxes of the natural sources were changing during this decade. The wetlands of the boreal taiga and tundra in the subarctic regions are some of the most abundant natural sources, producing CH_4 highly depleted in ^{13}C . Furthermore there is independent evidence of amplified warming of the arctic regions which could increase the areal extent of the wetlands and plausibly account for an increasing trend of fluxes of CH_4 , depleted in ^{13}C . This possibility is an important global environmental concern because of the positive feedback effect between the increasing concentration of atmospheric CH_4 , a greenhouse gas, and climate warming.

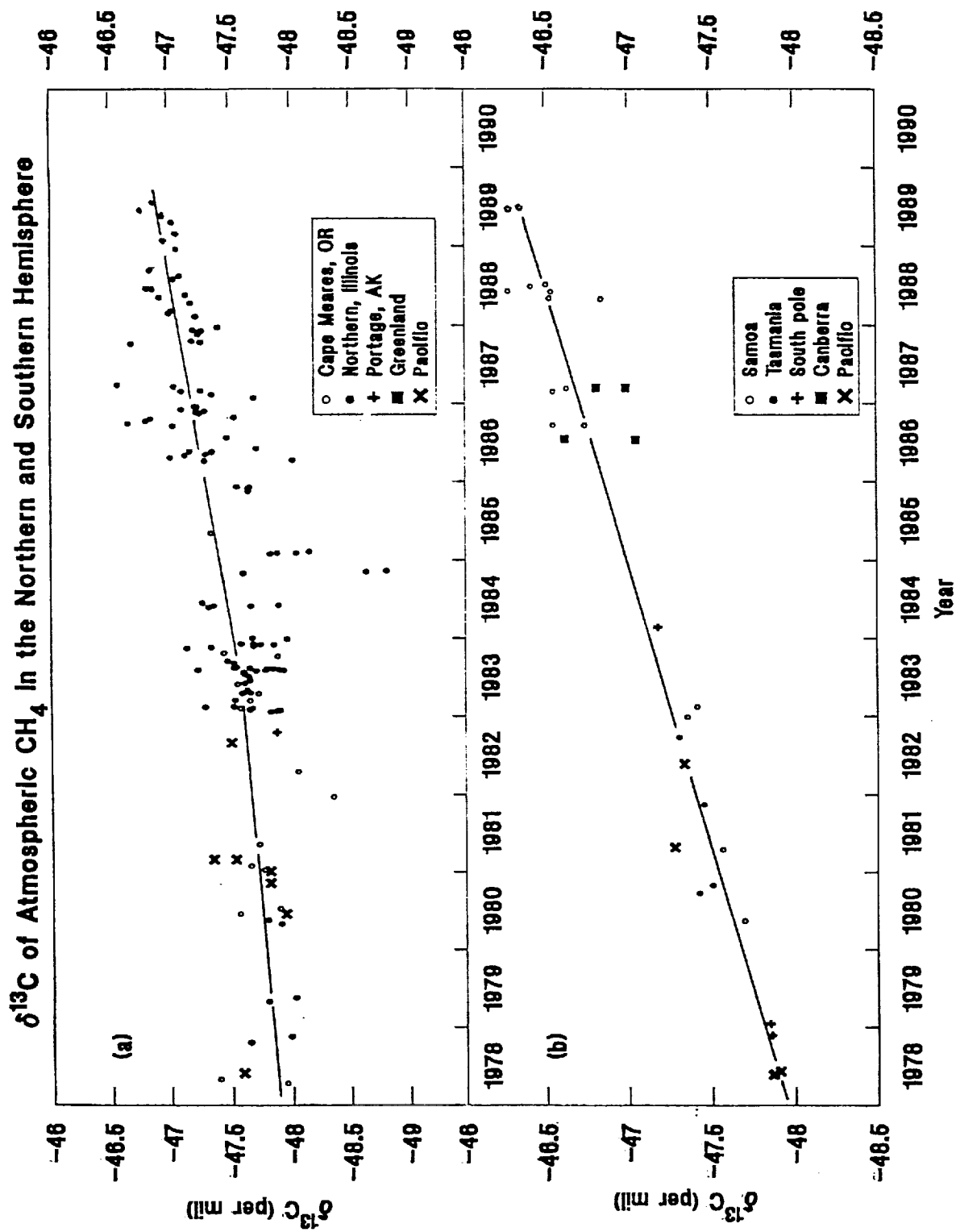
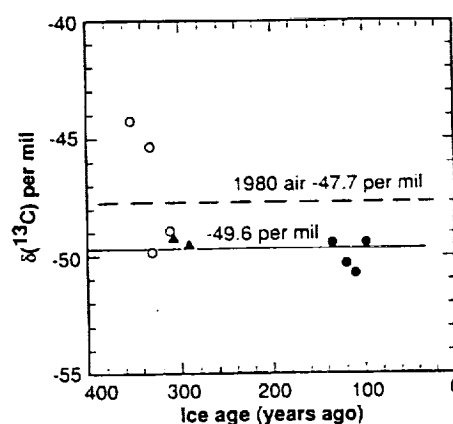


Fig. 1. The stable carbon isotopic composition of atmospheric CH_4 for both hemispheres from 1978 to 1989. The overall analytical error from sample processing and mass spectrometer analysis was less than ± 0.2 per mil for the individual data points.

Figure 2 shows the measurements of the isotopic composition of CH₄ in air contained in 100-300 yr old polar ice cores from two sites in Greenland. With the exception of two samples of "wafered" or highly fractured ice from the Dye 3 core, the ¹³C/¹²C ratio of the CH₄ is essentially independent of age and more depleted in ¹³CH₄ than the CH₄ in contemporary air by -2 per mil. The two anomalous results are attributed to fractionation during extraction of the gases by pumping. The concentration of atmospheric CH₄ from 300 years ago, representing only natural sources, has approximately doubled because of the addition of anthropogenic fluxes; the change in the isotopic composition due to the added anthropogenic fluxes is attributed to a greater flux of ¹³CH₄ from sources isotopically heavier than average CH₄, mainly from biomass burning, than from sources of isotopically light CH₄ such as rice paddies and herbivores. This result is consistent with the trend of increasing ¹³C/¹²C ratio observed in the last decade.

Fig. 2. The stable carbon isotopic composition, $\delta^{13}\text{C}$, of CH₄ in Greenland ice versus age of the enclosing ice. Triangles, samples from "Crete," Site A; circles, Dye 3 core samples; solid circles, solid ice; open circles, wafered ice. The estimated error of individual values is ± 0.7 per mil; the mean value of the 8 good samples is -49.6 ± 0.2 per mil.



Journal Publications

- Craig, H., C. C. Chou, J. A. Wehlan, C. M. Stevens, and A. Engelkemeir, The isotopic composition of methane in polar ice cores, *Science* **242**, 1535, 1988.
- Stevens, C. M., Atmospheric methane, *Chemical Geol.* **71**, 11-21, 1988.
- Stevens, C. M. and A. F. Wagner, The role of isotopic fractionation effects in atmospheric chemistry, *Z. Naturforsch.* **449**, 376-383, 1989.

RESEARCH TASK: NASA-NAGW-972

A. Title: **Carbon Isotopes in Polar Ice Core Methane**

B. Investigator: Harmon Craig
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, California 92093

C. ABSTRACT OF RESEARCH OBJECTIVES:

Program objectives were (1) a study of the variations in the isotopic composition of carbon in methane in trapped gases in ice samples from Greenland and Antarctica, (2) preparation of a system for extraction of gases from large volumes of ice (30 - 40 kg) for measurement of ^{81}Kr ages on the ice, and (3) a study of the processes responsible for oxygen supersaturation in the Antarctic "Dry Valley" Lakes, specifically Lake Hoare. The isotopic composition of carbon ($^{13}\text{C}/^{12}\text{C}$ ratio) reflects the varying proportions of the different sources of atmospheric methane during the past. We have shown that the effects of burning of tropical forests by humans during the past 50 - 60 years can be seen by changes in this ratio recorded in trapped methane in polar ice cores. We are also studying this ratio in blocks of ice in upwelling glaciers in Antarctica. This research is part of a larger program supported by the National Science Foundation. This NASA grant has provided partial support for Dr. Don Burtner, a Postgraduate Research Geochemist, funds for the assembly of a Krypton extraction system for polar ice, and support for analysis of gases trapped in the thick surface ice layer of Lake Hoare.

D. SUMMARY OF RESULTS:

We previously showed that the mixing ratio of methane in trapped gases in Greenland and Antarctic ice cores was about half the present value of 1.5 parts per million by volume ("ppmv") prior to about 350 years ago (H. Craig and C.C. Chou, Geophysical Research Letters 99, 1221, 1982). This finding has been confirmed in a number of other laboratories. More recently, under NSF support we found that the $^{13}\text{C}/^{12}\text{C}$ ratio in trapped methane in Greenland ice cores was 2‰ (parts per thousand) depleted in ^{13}C relative to present-day atmospheric methane from about 350 to 100 years ago. The recent increase in ^{13}C is attributed to effects of accelerated biomass burning and deforestation during recent decades. In the present study we have been analyzing methane in the upwelling Antarctic ice sheet in the Allan Hills, a section of the Transantarctic Mountain range, which is bringing up very old ice, perhaps 500,000 years or older. This ice has considerably higher $^{13}\text{C}/^{12}\text{C}$ ratios, lower CH_4 and air concentrations, and lower CH_4 mixing ratios. The composition of the trapped air is identical to that of the present atmosphere, showing that differential solubility effects in liquid water have not been significant. In 1988 we collected a systematic set of samples along and normal to the ice sheet flow during the Antarctic field season, and we are now studying many parameters in these ice samples. This work is being done in collaboration with C.M. Stevens and A. Engelkemeir of Argonne National Laboratory, who are responsible for the isotopic determinations, supported by NASA Grant W16188 to C.M. Stevens. A major problem has been the discovery that ice under pressure when brought to the surface expels different gases at different rates, due to capillary flow phenomena, which affects the relative composition of the trapped gases: this effect is under study at present.

Work is proceeding on the Kr extraction system. A major part of the system is being donated by Argonne National Laboratory, via our association with Dr. C.M. Stevens in the isotopic methane studies. A system previously used for collection of methane and krypton is being provided for our use in trapping and purifying the gases. The purified gases will then be shipped to our colleague Dr. R. Willis at Atom Sciences Inc., Oak Ridge, for measurement of the ^{81}Kr to total Kr ratio. This ratio is being measured by laser-based Resonance Ionization Spectroscopy, following isotopic enrichment of the ^{81}Kr . Since the half-life of ^{81}Kr is 210,000 years, this isotope is the best, and indeed the only, chance for dating ice beyond the range of ^{14}C (50,000 years). This method is just beginning to work, and it will be some years yet before dates can be measured. We are using the old Allan Hills ice to establish the method: this is the only source of old ice in the large quantities required at present for the method. We hope to measure ^{81}Kr in ~30 kg of recent ice and ~60 kg of ancient ice, greater than 100,000 years old. This is in the range of the samples we are using for the methane isotope measurements, and we hope for improvements by about a factor of two in the next few years.

The third part of this project was a contribution to a separate NASA supported program dealing with the ice-covered "Dry Valley" lakes of Victoria Land, in this case Lake Hoare, a perennially ice-covered lake supersaturated in both nitrogen and oxygen by large amounts. The study of gases in this lake has been a continuing study by R.A. Wharton and C.P. McKay of the Life Science Division, NASA-Ames Research Center. Our work on this lake came about because of our development of a method for separation of biological and physical contributions to O_2 supersaturation in oceans and lakes by simultaneous measurement of N_2 , O_2 , and Ar, using Argon as a surrogate for physical effects involved in the supersaturation of oxygen. By analyses of the gases trapped in the 4-5 meter layer of ice on the surface lake, we showed that the major loss of gases from the lake is by removal of gases trapped in the ice freezing on the surface, in the sublimation and ablation of this ice layer (which is renewed by flow of meltwater from glaciers into the lake). Our results show, that contrary to previous estimates based on indirect calculations and on N_2 and O_2 saturations alone, that 89% of the oxygen supersaturation is due to the physical process of ice freezing, while only 11% is due to photosynthesis in the lake. This result is inherently more reasonable than supposing that very large rates of oxygen production by photosynthesis could occur in a lake with such a thick perennial ice cover.

A paper has been completed on this work, and a proposal has been submitted to NSF, for sampling and analyzing lake water and ice samples to study respiration - photosynthesis effects in these unique polar lakes. NASA's interest in these ice-covered lakes lies in their use as possible models for the existence, at some stage, of liquid water on Mars.

E. PUBLICATIONS:

Abstract: "GRAVITATIONAL AND PRESSURE-RELEASE FRACTIONATION EFFECTS IN GREENLAND ICE CORES", by H. Craig, D. Burtner, and R.C. Wiens, EOS (Transactions of the American Geophysical Union), In Press for 1989 National Meeting.

Paper: "OXYGEN SUPERSATURATION IN AN ICE-COVERED ANTARCTIC LAKE: BIOLOGICAL VERSUS PHYSICAL CONTRIBUTIONS", by H. Craig, D. Burtner, R.A. Wharton Jr., and C.P. McKay, submitted to Science (1989).

A. Title

Geochemical Reaction Rate Studies on Microbial Aerobic Methane Oxidation, a Modulator of Atmospheric Methane Fluxes from Tundra and Marine Environments

B. Investigator and Institution

William S. Reeburgh (P.I.) and Stephen C. Whalen (Postdoc)
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University of Alaska Fairbanks
Fairbanks, Alaska 99775-1080

C. Research Objectives

1. Determine seasonal flux of methane from wet and dry tundra environments and measure the depth distribution of microbially mediated methane oxidation.
2. Determine the rate and depth distribution of methane oxidation in coastal and oceanic waters.

D. Progress and Results

Flux time series and transects. We have completed a three year time series of net methane flux from permanent sites in the University of Alaska Arboretum. Static chamber flux measurements are being made in triplicate at approximately weekly intervals on sites typical of large areas of arctic tundra: moss sites, *Eriophorum* tussocks, *Carex* stands, and "black holes", the unvegetated depressions surrounding the *Eriophorum* tussocks. Our field program is designed to document spatial and temporal variability in net methane fluxes from tundra systems and produce net emission rates suitable for incorporation into models. We are also measuring soil temperature distributions and water table levels. Our work indicates that tussock tundra is a more important methane emitter than previously believed.

We measured methane concentration (membrane equilibration samplers) and methane oxidation rates by soils (jar experiments on soil cores and soil core segments under ambient and enhanced methane atmospheres and with stable and labelled methane). We also measured methane flux along a detailed (10 km intervals) road transect from the Arctic Circle to Prudhoe Bay (500 km) during August, 1987.

An estimate of global methane emission by tundra was made by weighting our measured Arboretum site fluxes by site type coverage for wet and tussock tundra and applying these to total tundra area. An independent check was made using our road transect data, which are weighted by site type through the sampling strategy and involve assuming only emission period. Both estimates agree reasonably, 20 - 60 Tg/yr (2 years data) for the time-series data, and 38 Tg/yr for the transect data.

Regarding processes, vascular transport appears to be important in the *Eriophorum*

and *Carex* sites. Aerobic oxidation occurs at the water table and appears to be an effective control on fluxes from the moss and black hole sites. Sites with depressed water tables under dry conditions show greatly decreased methane fluxes. Vascular transport effectively bypasses this zone of oxidation, so fluxes from the *Eriophorum* and *Carex* sites are less sensitive to water table level. Our time series includes a year with normal precipitation and one with half the long-term mean.

Soil Oxidation. We have performed jar and chamber experiments on aerobic methane oxidation. Methane oxidation in most of the tundra sites does not exceed production, so net flux to the atmosphere occurs. We encountered two sites, one at Skan Bay in the Aleutian Islands and another at the Berkeley, California, landfill that gave spectacular methane consumption results. Soils at both sites consumed chamber and jar headspace methane to concentrations well below ambient atmospheric levels (0.1 ppm), in 8 hours and 1 hour, respectively, suggesting that soils function not only as a flux modulator, but also as sinks for atmospheric methane. We were able to isolate the methane oxidizing organism from the Berkeley landfill and have performed kinetic experiments. We are currently using Münnich and Dörr's radon method to transport-correct fluxes and learn more about the role soil resistance plays in equilibration and transport from the atmosphere.

Oceanic measurements. We participated in a cruise to the Black Sea in 1988 and successfully applied a newly-developed tracer method involving tritium-labeled methane in water column methane oxidation rate measurements. This tracer has the advantage of extending the sensitivity of rate measurements about 100-fold over measurements using radiocarbon-labeled methane tracer. Our experiments covered oxidation under both oxic and anoxic conditions.

Present and Future Work. Our continuing support will permit continuing the tundra flux time-series, adding additional sites in the Taiga LTER site at Bonanza Creek, and further studies on the importance of aerobic methane oxidation. The LTER collaboration provides access to an established set of sites, expert colleagues and a variety of environmental data obtained routinely at the control sites. We will expand the gases measured to include CO, N₂O and CO₂.

E. Journal Publications

Whalen, S. C. and W. S. Reeburgh. 1988. A methane flux time-series for tundra environments. *Global Biogeochemical Cycles* 2(4):279-288.

Sandbeck, K. A. and W. S. Reeburgh (accepted and in press) Microbiological preparation of ³H-labelled methane. *J. Labelled Compounds and Radiopharmaceuticals*.

Whalen, S. C. and W. S. Reeburgh (accepted and in press) A methane flux transect along the Trans-Alaska Pipeline Haul Road. *Tellus*.

TITLE: Investigation of Relationship Between Soil Biogeochemistry and Methane Generation in Panamanian Tropical Ecosystems

INVESTIGATORS: Dr. Robert F. Stallard (PI), U.S. Geological Survey-Water Resources Division, Box 25046 DFC MS-413, Lakewood, CO 80225

Mr. Michael Keller (graduate student), Princeton University, Princeton NJ, 08544.

ABSTRACT OF RESEARCH OBJECTIVES:

A 2-year-long systematic study of methane emission from Panamanian soils was completed at the end of 1988. The objectives were to (1) quantify sources and sinks of methane, (2) describe diel and seasonal patterns of production and consumption, (3) identify phenomena that are important to the methane budget, (4) evaluate the effects of land-use changes upon going from the natural to a developed state, and (5) address the question: is development in the tropics important to past and future changes in the methane budget? Study sites were located near to the field laboratories of the Smithsonian Tropical Research Institute (STRI), with special emphasis on one locality, Barro Colorado Island Nature Monument (BCI). Fieldwork consisted of continuous monitoring of the project's 9 study localities by a graduate student, Michael Keller, from Princeton University, and several complex, month-long, experiments involving the coordinated efforts of researchers from U.S. Geological Survey (USGS), STRI, and the National Center for Atmospheric Research (NCAR).

SUMMARY OF PROGRESS AND RESULTS:

This is among the first studies to quantify the seasonality of methane emission in tropical habitats. Wetlands are a major source ($>100 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$), and soils of moist and dry forests are a ubiquitous sink ($-1 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$). Swampy soils, with a water table of less than about 40 cm depth, release methane to the atmosphere. When the soils dry, emission ceases within days.

Forest Soils and Methane Consumption:

An in vitro incubation technique was used to determine the capacity of various soil layers to consume methane and to study the effects of agricultural development on forest soils. Samples came from a tropical moist forest and from two pastures and an upland rice field that had been converted from forests. Consumption of methane by forest soils was significantly greater than by soils from agricultural land at all depths. In forest soils, the greatest methane consumption occurred in the top 10 cm, whereas in the two pastures and the rice field the greatest consumption took place in the 10- to 20-cm depth interval. Field measurements from flux chambers confirm the results of the in vitro experiments and indicate that fluxes into agricultural soils are about 20 to 40 percent of those into forest soils.

Wetlands and Lakes and Methane Production:

Floating enclosures were used to measure methane fluxes out of wetland and lake habitats. These measurements indicate that wetland and lake habitats emit 100 to $300 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

Studies on Lake Gatún, Panama, using arrays of continuously deployed funnel collectors, show that ebullition of methane from shallow waters (<5 m depth) is the predominant mechanism of methane emission from the lake to the atmosphere. At shallow water sites, total ebullition emissions ranged 100 to $2000 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and averaged about $500 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. In waters deeper than about 5 m the rate of ebullition seems diminished to about $100 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. Bubbling often occurred episodically. At some sites, bubbling events of less than 2 hours duration released more than 90 percent of the daily methane emission. Wind driven waves seemed to force these bubbling episodes.

Effect of Development on the Methane Budget of Panama Canal Basin

Although this research was process oriented, efforts were made to evaluate the effect that human activities have had on the methane budget for the Panama Canal drainage basin. Two classes of activities are important: agriculture and hydrologic development. Agricultural development reduces the methane consumption by soils by 20 to 40 percent. The building of the Canal involved the creation of large lakes and the replacement forest soil sinks by strong sources. The effect of human activities has been to shift the Panama Canal Basin from a condition involving an approximate balance between production and consumption of methane to a condition of strong net production on the order of $10 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

JOURNAL PUBLICATIONS:

Keller, M., Mitre, M. E., and Stallard, R. F., Consumption of atmospheric methane in tropical soils: Effects of agricultural development, submitted to Science.

Keller, M. and Stallard, R. F., Two methods for measuring methane emission from a tropical lake, submitted to Limnology and Oceanography.

RESEARCH SUMMARY

A. Title of Research Task:

Methane and Carbon Monoxide: Flux and Microbial Process Studies in Streams, Rivers and Coastal Marine Ecosystems.

B. Investigator and Institution:

Marvin D. Lilley
School of Oceanography
University of Washington

C. Abstract of Research Objectives:

The flux of methane to the atmosphere from streams and rivers is poorly known. This investigation is designed to quantify these fluxes and to evaluate what chemical and physical variables are important in controlling the microbial production and consumption of methane in streams in temperate forested watersheds.

D. Summary of Progress and Results:

Since the last summary, we have conducted two sampling trips to the Columbia River, the second largest river in the U.S. with a drainage basin of 670,810 km² and an average annual discharge of 8,267 m³s⁻¹. These trips were made in Oct. 88 and June 89 and cover the high and low flow periods of the river. The average methane concentration in the lower 400 km of the river was 239 nM resulting in an average flux of 10 mg m⁻² d⁻¹ to the atmosphere. Methane concentrations decrease dramatically in the estuary and appear to be controlled by the mixing of low methane sea water with high methane river water.

Incubation experiments conducted to determine the rates at which methane was oxidized microbially within the riverine water column showed that the rates typically ranged from 10 to 20 nM d⁻¹. Thus, in the river above the estuary, microbial oxidation removes about 25% of the standing crop of methane, while the remainder is evaded to the atmosphere. However, in the estuary, the rates of oxidation dropped off very rapidly as salinity increased, and where salinities greater than 10 ppt were encountered, the rates were typically in the .02 to .05 nM d⁻¹ range. To evaluate whether this dramatic reduction in oxidation rates was simply a salinity effect or due to some other factor, we conducted experiments in which river water was amended with either filter sterilized high salinity water or with NaCl and evaluated the impact on the oxidation rates. These experiments showed that both treatments resulted in a similar reduction in rates for a given salinity, indicating that the salinity increase does result in stopping methane oxidation by fresh water organisms in the estuary and our data also indicate that, at least within the estuary, a marine organism does not rapidly replace this function which possibly results in most of the riverine methane which reaches the ocean being subsequently evaded to the atmosphere.

Our continuing work on the Wenatchee River, a tributary of the Columbia River on the eastern slopes of the Cascade mountain range has shown that along-stream variability in any given season is greater than seasonal variability at a given stream site. This is primarily a function of the geomorphology of the streambed in that the Wenatchee consists of a series of alternating reaches of pools, riffles, and rapids. Methane concentrations build up in the pool areas and are released to the atmosphere in the riffles and, particularly, in the rapids where whole-stream mixing is vigorous. In the Wenatchee, a clear mountain stream, we see methane flux values in the rapid areas below pools approaching $200 \text{ mg m}^{-2} \text{ d}^{-1}$. These rates are comparable to the higher levels seen at most wetland systems studied to date.

In addition, we evaluated the increased flux of methane as a result of physical mixing induced by barriers such as spillways and waterfalls. At a small spillway on the Wenatchee River (5 m tall), the resultant loss of methane was $5 \times 10^6 \text{ g yr}^{-1}$. At a 70 m falls on the Snoqualmie River ($73.5 \text{ m}^3 \text{ s}^{-1}$ flow) on the western slopes of the Cascades, a flux of $4 \times 10^7 \text{ g CH}_4 \text{ yr}^{-1}$ was measured. A continuing part of this work will be to evaluate the significance of rapids, waterfalls and hydroelectric dams on the methane flux from lotic systems.

E. Journal Publications:

1. Lilley, M.D., J.A. Baross, and C.N. Dahm, Methane Production and Oxidation in Lakes Impacted by the May 18, 1980 Eruption of Mt. St. Helens. *Global Biogeochemical Cycles*, 2: 357-370, 1988.
2. The work described here was presented at the 24th Congress of the International Association of Theoretical and Applied Limnology, Aug. 13-19, Munich, FRG, and will be published in early 1990.

Research Summary: Methane Oxidation in the Open Ocean

Principal Investigator: B. B. Ward
Award No.: NAGW-837
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Scripps Institution of Oceanography
University of California, San Diego
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5 August 1989

Abstract of Research Objectives

The ocean is a small net source of methane to the atmosphere. Surface waters are generally supersaturated, and a subsurface concentration maximum is typically observed. The balance between the air/sea flux and the supply of methane to surface waters by diffusion from the maximum requires the existence of an in situ production process. Biological production and consumption processes are assumed to control the distribution of methane in the ocean, but the source of methane in the surface ocean has not been identified. This project addresses the consumption of methane through biological oxidation, and thereby allows us to estimate indirectly the required magnitude of the production process. The goals of the project are 1) to measure methane distributions and oxidation rates in ocean waters and 2) to use this information to calculate net consumption terms and estimate fluxes between ocean and atmosphere.

Summary of Progress and Results

During 1988, three research cruises were undertaken in pursuit of the above outlined goals. The last one occurred in October 1988 in conjunction with NSF-supported research on related topics. Results are presently being analyzed and manuscripts are in progress. Preliminary findings are consistent with the expected observation of a subsurface methane concentration maximum which is not consistently correlated with other water column features such as light or chemical distributions. Methane oxidation rates associated with the subsurface maximum were detectable but low, implying very slow turnover of the methane pool. Very low rates made it difficult to distinguish possible effects of various environmental variables on methane oxidation rates. We can state at this point that there is no effect of added nitrogen, but there may be a light/dark effect. Attempts to measure methane accumulation in incubated samples detected only net methane consumption. Funding for this project terminated in March 1989. Manuscripts are being prepared from results obtained in the Southern California Bight and the Black Sea in 1988.

Journal Publication

Ward, B. B., K. A. Kilpatrick, A. E. Wopat, E. C. Minnich and M. E. Lidstrom. 1989. Methane oxidation in Saanich Inlet during summer stratification. *Continental Shelf Research*, 9: 65-75.

Ward, B. B. and K. A. Kilpatrick. Relationship between substrate concentration and oxidation of ammonium and methane in a stratified water column. Submitted to *Continental Shelf Research*.

NASA 1988-89
Biennial Research Summary

A. Title: Isolation and Characterization of Methanotrophs Capable of Growth at Low Methane Concentrations.

B. Principal Investigators:

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C. Abstract:

Laboratory and field studies were carried out to assess the role of methanotrophs in low methane, low flux environments and to make comparisons to other methane consumption systems. We developed and tested immunological and EM techniques for the detection of methanotrophs in natural samples. These techniques are important in assessing natural populations. Secondly, we determined methane and oxygen profiles, distributions of methane consumption activity and kinetic parameters for seven distinctly different environments, ranging from low to high methane. Our conclusions from these field experiments are that methane consumption is stratified at oxic/anoxic boundaries, in agreement with data from other environments; that methane consumption rates and probably populations of methanotrophs are usually methane-limited and can be correlated with the magnitude of the methane flux to the oxic/anoxic interface; and that in one case in which steady-state methane concentrations were low (10 nM), the populations showed a correspondingly high affinity for methane.

D. Summary of Progress and Results:

a) Isolation and Characterization of Methanotrophs.

Pure cultures were isolated from Lake Superior, Menomonee River, Saanich Inlet, The Galapagos and the Gulf of Mexico. Enrichment cultures currently being worked are from Panama and Alaskan tundra soil samples, water samples from Lake Michigan, Lake Baikal (USSR), the Black Sea, Princess Louisa Inlet, hydrothermal vents from Yellowstone Lake and the Galapagos, and cold water seeps from the Gulf of Mexico.

b) Measurements of Methane Oxidation In Situ.

K_m values for the 7 different aquatic environments fall within the range of 1.2 to 12 μM except at Saanich Inlet and the Black Sea. For Saanich Inlet, the K_m value was an order of magnitude lower (0.3 μM). This low K_m value was correlated with correspondingly low methane fluxes and methane levels. V_{max} values correlated roughly with the flux of methane to the zone of highest methane oxidation. Highest oxidation rates were concentrated at the oxic/anoxic interface.

c) Assessment of In Situ Populations.

Using Percoll gradients to determine buoyant density, we were able to show that Type I and Type II methanotrophs are easily separated and that this distinction is consistent regardless of growth state or accumulation of storage products. We were able to use this successfully as a rapid method for selective enrichments of methanotrophs from natural samples.

We have examined the ultrastructure of a large number of Type I and Type II methanotrophs by traditional TEM and SEM techniques, as well as less traditional methods such as freeze-fracture and various cytochemical techniques. This work will be described in a forthcoming review paper on the ultrastructure of methanotrophs.

Antibodies directed against specific enzymes or specific outer cell antigens have proven useful in assessing natural populations. Using whole cell antisera against two strains of methanotrophs, we developed an indirect fluorescent antibody staining technique to enumerate methanotrophs in natural aquatic samples. In Menomonee River waters, an in situ population of ca. 2000 methanotrophs/ml was determined from a total bacterial population of 10^7 /ml, or a ratio of 1:10,000.

Finally, antisera against Methylobacterium albus BG8 methanol dehydrogenase (MDH) and Methylobacterium sp. strain AML MDH were used in combination with an EM-immuno-gold procedure for the detection of MDH in bacteria from natural samples.

E. Journal and Abstract Publications:

1. Kuivila, K.M., J.W. Murray, A.H. Devol, M.E. Lidstrom and C.E. Reimers. 1988. Methane cycling in the sediments of Lake Washington. *Limnol. Oceanogr.* 33:571-581.
2. Remsen, C.C. and L.A. Buchholz. 1988. Aerobic methane oxidation in the Black Sea. *EOS, Trans. AGU* 69:(44)1240.
3. Fassel, T.A., L.A. Buchholz, M.E. Lidstrom, M.J. Schaller and C.C. Remsen. 1988. Indirect immunogold labeling of methanol dehydrogenase in a methanotrophic bacterium. *Proc. 46th Ann. EMSA*, 376-377.
4. Fassel, T.A., M.J. Schaller and C.C. Remsen. 1988. Ruthenium red and alcian blue effects on outer structures of methanotrophic bacteria. *Proc. 46th Ann. EMSA* 74-75.
5. Putzer, K., T.A. Fassel and C.C. Remsen. 1988. Enhancement of outer cell layers of a methanotrophic bacterium using uranyl acetate en bloc. *Proc. 46th Ann. EMSA* 72-73.
6. Lidstrom, M.E. 1988. Molecular approaches to problems in biogeochemical cycling. *Ant. v. Leeuwenhoek* 54:
7. Remsen, C.C., E.C. Minnich, R.S. Stephens, L.A. Buchholz and M.E. Lidstrom. 1989. Methane oxidation in Lake Superior Sediments. *J. Great Lakes Research*, 15:141-146.
8. Ward, B.B., K.A. Kilpatrick, A.E. Wopat, E.C. Minnich and M.E. Lidstrom. 1989. Methane oxidation in Saanich Inlet during summer stratification. *Continental Shelf Res.* (In Press).
9. Fassel, T.A., M.J. Schaller, M.E. Lidstrom and C.C. Remsen. 1989. Influence of fixation-resin combinations and ruthenium red in elucidating surface and ultrastructure of methanotrophic bacteria. *J. Electron Microscopy Tech.* (In Press).

A. Title of Research Task

" ^{13}C in Atmospheric Methane and its Sources", NASA contract W-16,184

B. Investigators and Institutions

Ralph J. Cicerone, P. I., National Center for Atmospheric Research, Boulder, Colorado
Stanley C. Tyler, National Center for Atmospheric Research, Boulder, Colorado

C. Abstract of Research Objectives

We proposed a three-year research program beginning in 1986 to measure the $^{13}\text{C}/^{12}\text{C}$ ratio in atmospheric methane and in methane gathered from sites and biota that appear to be major sources of atmospheric methane. The purpose of this research is to use ^{13}C signatures to identify major sources of atmospheric methane, a necessary step toward understanding why methane concentrations are increasing globally. Efforts have been focused on rice agriculture, termites, and swamps and marshes as sources.

D. Summary of Progress and Results

Results.

Much of our work has concentrated on better characterizing some specific CH_4 sources to determine methods of production and consumption of methane. The sources so studied include tropical wetlands in Panama, and termite mounds, rice paddies, and papyrus swamps in Kenya. Tropical rain forest sources have been studied by taking samples seasonally in selected sites such as mangrove swamps, permanent marsh areas with both floating and rooted aquatic plants and grass, and seasonal swamp areas in a floodplain area along the Rio Chagres. Plants and organic material making up the decaying matter in these sites have also been collected for $\delta^{13}\text{C}$ analysis. Our research in Panama includes a collaboration with Dr. Robert Stallard of the USGS in Denver (who is also working on a project in Panama). We collaborated with Stallard and his graduate student Michael Keller to study both uptake of methane on dry and wet forested soils and the bottom sediment bubbles from lake and shallow marsh areas (which compliment the surface emissions taken using enclosures). The preliminary experiments done with wet and dry soils indicate that the soil bacteria greatly fractionate methane and that uptake of methane occurs on both types of soils.

Analysis of a field experiment in Kenya was completed and the results published in 1988. Measurements of termite methane from mounds were made and analyzed in conjunction with samples of termite bodies, forage, and fungus combs as well as CO_2 gas produced by the termites. Papyrus marsh samples were collected to study methane emissions from a wetland environment known to contain C-4 type plants. Rice paddy fields in Kenya were systematically studied to correlate methane emissions with rice variety and time elapsed between sowing and sampling during the growth cycle.

We also made a redetermination of the fractionation effect of gas-phase OH radical attack on CH_4 , the principal sink for methane molecules in the atmosphere, in collaboration with the Atmospheric Kinetics and Photochemistry group here at NCAR. Our new value for the fractionation effect at room temperature is more precise than the old value reported in Davidson et al. We also have data for the temperature dependence of the reaction.

A great deal of new information about atmospheric methane has become available in the last several years, much of it due to NASA's program. We have critically examined all

available data and we have constructed a new budget of global methane sources; isotope data provided key constraints.

Progress.

Our current research stems from a new NASA contract entitled "Isotopic Studies of Atmospheric Methane: Factors Controlling Methane Consumption and Production". S. C. Tyler is the principal investigator and R. J. Cicerone is the co-investigator. We have begun to monitor ^{14}C , and $^{13}\text{C}/^{12}\text{C}$ ratios in clean air sites at Niwot Ridge, Colorado to compare to ongoing work at Baring Head, New Zealand. Recent work by both Lowe and co-workers at Baring Head and M. Wahlen at Lamont Doherty in New York indicates that fossil fuel or "dead" methane sources may account for as 20-32% of the total methane emissions to the atmosphere in recent years. By using the above-mentioned isotopes, we hope to investigate this possibility further. This aspect of our research brings up an interesting possibility that has received no attention up to now. Are some of the biogenic sources of methane ^{14}C -depleted? It may be that old deposits of peat or tundra areas for example are contributing methane to the ^{14}C signal which is being mistaken as evidence for additional sources of fossil fuel or geothermal methane. We have begun to investigate possible sources of "dead" methane in two ways. We recently completed a study of CH_4 and CO emissions from asphalt pavement. The data and analysis are ready to be submitted. We have also just begun to analyze emissions collected from northern peat wetlands in Canada during 1989. We anticipate that gases such as CH_4 and CO_2 released from this source may be produced in part from older carbon reservoirs depleted in ^{14}C .

E. Journal Publications

Cicerone, R. J., and R. Oremland, "Atmospheric Methane and the Biosphere/Geosphere: An Overview", *Global Biogeochemical Cycles*, Vol. 2, No. 4, pp. 299-327, 1988.

Tyler, S. C., P. Zimmerman, C. Cumberbatch, J. Greenberg, C. Westberg, and J. P. E. C. Darlington, "Measurements and Interpretation of $\delta^{13}\text{C}$ of Methane from Termites, Rice Paddies, and Wetlands in Kenya", *Global Biogeochemical Cycles*, Vol. 2, No. 4, pp. 341-355, 1988.

Cicerone, R. J., "The Hole in the Ozone Layer", *Science Year 1989*, pp. 76-89, World Book, Inc., Chicago, Ill., 1988.

Cicerone, R. J., "Methane Linked to Warming", (invited), *Nature*, Vol. 334, p. 198, 1988.

Tyler, S. C., " $^{13}\text{C}/^{12}\text{C}$ Ratios in Atmospheric Methane and Some of Its Sources", (invited), *Springer-Verlag Ecological Studies Series*, edited by J. Ehleringer, K. Nagy, and P. Rundel, Springer-Verlag Publishers, New York, Vol. 68, Ch. 22, pp. 395-409, 1989.

A. Title: Methane Processes in Wetlands and Forest Soils: Production, Decomposition, and Emission

B. Investigators: Gerald E. Lang, Joseph B. Yavitt, Alan J. Sexstone
West Virginia University, Morgantown, WV 26505

Daniel M. Downey
James Madison University, Harrisonburg, VA 22807

C. Objectives:

This research program was designed to assess the role of Sphagnum-dominated wetlands and coniferous forest soils as biogenic sources of methane. Our efforts were focused on the functional roles of methane production and methane oxidation as key processes affecting the amount of methane emitted to the atmosphere from wetland surfaces and forest soils. Complementary laboratory and field measurements were designed to address the following objectives separately in both wetland peat and coniferous forest soil:

1. To determine the potential rate of microbial methane production and methane decomposition as mediated by methane-oxidizing bacteria;
2. To document seasonal changes in the concentration of: methane, acetate, hydrogen gas, carbon dioxide, and oxygen; and
3. To estimate the rate of methane emission to the atmosphere.

D. Progress and Results:

Control of Methane Fluxes

1. In each of the six wetland plant community types that were sampled, the greatest rate of potential methane production occurred in the top 10-cm of the peat, and rates decreased with increasing depth in the peat; 60 to 75% of the production of methane occurred in the root zone (0 to 10-cm depth).
2. Potential methane production is greatest in the late autumn months regardless of the plant community. Maximum rates of production approached $25 \text{ } \mu\text{mol h}^{-1}$ in the 5-10 cm depth within the peat profile.
3. Potential methane production can vary by an order of magnitude among the six different wetland plant communities. The lowest values ($0.9 \text{ mmol m}^{-2} \text{ h}^{-1}$ [June value]) were found in the Sphagnum-bog community while the highest values ($6.2 \text{ mmol m}^{-2} \text{ h}^{-1}$ [June value]) were measured in the sedge-meadow community.
4. Potential methane production is enhanced in plant communities with extensive sedge cover; the following species were important in Appalachian peatlands: Rhynchospora alba, Eriophorum virginicum, Carex canescens, and Carex folliculata.

5. Much of the potential methane production is consumed in situ in the peat by aerobic methane oxidizing-bacteria. The maximum rate measured was $18.7 \text{ } \mu\text{mol h}^{-1}$; most values ranged from 0.1 to $9.9 \text{ } \mu\text{mol h}^{-1}$.
6. The mean rate of methane emission from wetland communities averaged $25 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, with daily mean values ranging from -25 to $100 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$.
7. Under field conditions in wetlands, the overall amount of methane emitted to the atmosphere is higher in summer than in winter.
8. On a diurnal basis, methane emission from the peat to the atmosphere is highest in early morning.
9. Trace amounts of methane production were measured in forest soils under laboratory incubations, primarily in the L and F horizons.

Patterns Across Complex Landscapes

1. Methane emission is characterized by high spatial variability within a wetland community, between communities, and among wetlands.
2. Methane consumption by forest soils appears to be a universal phenomenon.
3. Wetlands are net sources of atmospheric methane and carbon dioxide, whereas forest soils are net sinks for methane.

E. Publications (1988-1989):

1. Yavitt, J.B., G.E. Lang, and D.M. Downey. 1988. Potential methane production and methane oxidation rates in peatland ecosystems of the Appalachian Mountains, United States. *Global Biogeochemical Cycles* 2:253-268.
2. Yavitt, J.B., D.M. Downey, E. Lancaster, and G.E. Lang. 1989. Methane consumption in decomposing Sphagnum-derived peat. *Soil Biology and Biogeochemistry*. In Press.
3. Yavitt, J.B., D.M. Downey, A.J. Sexstone, and G.E. Lang. 1989. Methane consumption in two temperate forest soils. *Biogeochemistry*. In Press.
4. Sexstone, A.J. and C.N. Mains. 1989. Production of methane and ethylene in organic horizons of spruce forest soils. *Soil Biology and Biogeochemistry*. In Press.
5. Wieder, R.K., J.B. Yavitt, and G.E. Lang. Methane production and sulfate reduction in two Appalachian peatlands. *Biogeochemistry*. In Review.

RESEARCH SUMMARY

SOURCES OF ATMOSPHERIC METHANE FROM NORTHERN PEATLANDS

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Research Objectives:

Northern peatlands are the source of approximately 50-60% of global atmospheric methane derived from wetland ecosystems. Under present climatic conditions methane production in northern tundra and boreal peatlands results primarily from microbial decomposition of near surface organic materials. In the Arctic additional reservoirs of methane exist trapped in terrestrial permafrost and in frozen hydrate forms below the continental shelves.

Our project has two primary objectives. First, we are developing, with other investigators in the NASA program, methods for improved quantitative estimates of methane emissions from wetlands at landscape to regional scales. Second, we are investigating relationships between soil climate (e.g., temperature, moisture) and methane emissions to provide insights into potential feedback mechanisms associated with wetland ecosystem response to climatic change.

Summary of Progress and Results:

The NASA Global Tropospheric Experiment/Arctic Boundary Layer Expedition (GTE/ABLE-3A), which included our team funded by UARP/IDP, completed a remarkably successful large-scale methane flux experiment in summer, 1988. A combination of enclosure/satellite, micrometeorological tower, and airborne flux measurement techniques were used in an experiment to quantify methane sources in the Yukon-Kuskokwim tundra landscape in Alaska. This first intercomparison of these three approaches to methane flux determination indicated that all methods could independently produce similar estimates ($\pm 10-20\%$) of the landscape methane source strength. The ABLE-3A also demonstrated that integration of all three techniques in a coordinated measurement program can produce quantitative estimates of methane flux over a wide range of time and space scales. These results are critical to planning future experiments for early detection of climate change in northern ecosystems.

Comparison of our results from tundra and boreal peatlands suggests that soil moisture is the dominant factor controlling methane emissions from tundra during warm periods, and soil temperature is the dominant factor in determining methane emissions from boreal peatlands of northern Minnesota. These field data provide a basis for preliminary modeling of the response of certain types of wetland ecosystems to a changing climate.

Publications:

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar, and W. Sanner, Methane flux from Minnesota peatlands, Global Biogeochem. Cycles, 2, 371-384, 1988.

Wilson, J.O., P.M. Crill, K.B. Bartlett, D.I. Sebacher, R.C. Harriss, and R.L. Sass, Seasonal variation of methane emissions from a temperate swamp, Biogeochem., 8, 55-71, 1989.

VI. ASSESSMENTS, COORDINATION, MISCELLANEOUS

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DATA SURVEY AND EVALUATION

W. B. DeMore
Jet Propulsion Laboratory

This task supports JPL participation in the

NASA PANEL FOR DATA EVALUATION

Chairman: W. B. DeMore, Jet Propulsion Laboratory

Panel Members:

- D. M. Golden, SRI International
- R. F. Hampson, National Institute of Standards
and Technology
- C. J. Howard, NOAA Environmental Research Laboratory
- M. J. Kurylo, National Institute of Standards
and Technology
- M. J. Molina, Jet Propulsion Laboratory
- A. R. Ravishankara, NOAA Environmental Laboratory
- S. P. Sander, Jet Propulsion Laboratory

Objectives:

The purpose of this task is to maintain an updated set of evaluated rate constants and photochemical cross-sections for use in stratospheric modeling, and to publish the evaluated data in a form accessible to the community of atmospheric scientists.

Progress and Results:

Preparations have been made for publication of Evaluation Number 9, expected in January of 1990.

Publications:

A series of eight evaluations has been published since 1977, the most recent being Evaluation Number 8, September, 1987, JPL Publication 87-41.

JANAF THERMOCHEMICAL TABLES FOR SPECIES OF INTEREST TO OZONE DEPLETION

Malcolm W. Chase
Principal Investigator
Standard Reference Data
and

Stanley Abramowitz
Chemical Thermodynamics Division
National Institute of Standards and Technology
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Abstract of Research Objectives

This critical evaluation focuses on the need for reliable thermodynamic data on the reactants and products involved in upper atmosphere chemistry. Of primary importance is the study of chemical species involved in the ozone depletion problem. The thermodynamic data will be provided in the format of the JANAF Thermochemical Tables. From a general standpoint, the preparation of such tables has had a long history and can be viewed as work continuing beyond the most recent JANAF compilation, i.e. JANAF Thermochemical Tables - 3rd edition, J. Phys. Chem. Ref. Data 14, Supplement No. 1, 1985. This work is to be provided to NASA in four steps: annotated bibliographies, tabular summaries of the available data, preliminary thermochemical tables for comment within the NASA community, and final tables (after NASA approval) for publication in the Journal of Physical and Chemical Reference Data.

Summary of Progress and Results

For FY89, the initial effort concentrated on the construction of annotated bibliographies for six chemical species, and their possible ions. A complete literature survey was conducted for ozone, atomic chlorine, and six gaseous chlorine oxides - ClO , ClO_2 , OClO , ClOO , $(\text{ClO})_2$, and Cl_2O . Information was also collected, if available, for the positive and negative ions of these species. These bibliographies are to be forwarded to NASA for comment and then published as a NIST Technical Note. The spectroscopic information of these species is particularly important in that it is these data which are used to calculate the thermodynamic properties. Since the temperature range of prime interest for the upper atmosphere is 200 - 500 K, it is important to ensure the identification of all low-lying electronic energy states. Tabular summaries are being prepared for the vibrational frequencies and electronic energy levels of the polyatomic molecules and the vibrational-rotational levels and electronic energy levels for the diatomic molecules. For both types of molecules, the enthalpy of formation and/or bond dissociation energy information is also being summarized.

Journal Publications

The annotated bibliographies and data summaries are being printed for NASA approval and will be sent through the NIST editorial review board for publication as NIST Technical Notes. These should be published during early 1990. Preliminary tables will be available by February 1, 1990.

Chemical Kinetics Data Evaluation Activities
In Support of the NASA Upper Atmosphere Research Program

R. F. Hampson

Chemical Kinetics Division

National Institute of Standards and Technology

Gaithersburg, MD 20899

Objective

To provide the reliable, evaluated reaction rate data base required as input data for large scale modeling efforts which form the basis for our understanding of the complex interactive chemistry of the atmosphere.

Summary of Progress and Results

The principal investigator has participated in the data evaluation activities of the NASA Panel for Data Evaluation on which panel he has the primary responsibility to review and evaluate the rate data for reactions of halogen-containing species. Updated and reevaluated data bases were presented at meetings of this panel held in May 1989 and August 1989 to prepare Panel Evaluation Number 9.

The principal investigator also participated in the data evaluation activities of the IUPAC Commission of Chemical Kinetics Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Updated and reevaluated data bases were presented at meetings of this panel held in April 1988 and May 1989.

Publications

W. B. DeMore, D. M. Golden, R. F. Hampson, C. J. Howard, M. J. Kurylo, M. J. Molina, A. R. Ravishankara, and S. P. Sander, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," Evaluation No. 8 of the NASA Panel for Data Evaluation, JPL Publication 87-41. Jet Propulsion Laboratory, Pasadena, CA, September 1987.

R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III", IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem. Ref. Data 18, 881-1097 (1989).

R. F. Hampson and W. G. Mallard, "Databases for Atmospheric Chemistry" Proceedings of the 11th International CODATA Conference (September 1988, Karlsruhe, West Germany), CODATA Secretariat, Paris (1989).

R. F. Hampson, M. J. Kurylo, and S. P. Sander, "Evaluated Rate Constants for Selected HCFC's and HFC's with OH and O(¹D)" Prepared for the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), UNEP/WMO Special Report (1989).

Research Summary

A. Title of Research Task: Global Changes in Biogeochemical Cycles in Response to Human Activities.

B. Principal Investigator: Berrien Moore
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Charles Vorosmarty
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UNH

C. Abstract of Research Objectives: The main objective of our research remains the characterization of global biogeochemical cycles in both terrestrial and aquatic ecosystems. This characterization applies to both natural ecosystems and those disturbed by humans. The primary elements of interest are carbon and nitrogen, and our analysis seeks to quantify standing stocks and dynamic cycling processes. The translocation of major nutrients from the terrestrial landscape to the atmosphere (via trace gases) and to fluvial systems (via leaching, erosional losses, and point source pollution) are of particular importance in this study.

D. Summary of Progress and Results: Our work is organized around the construction and testing of component biogeochemical models which treat terrestrial ecosystem processes, aquatic nutrient transport through drainage basins and trace gas exchanges. We have made substantial progress over the last year in developing each of these models.

In order to more carefully analyze this suite of dynamic spatial models, we have expended considerable effort during the last year in standardizing techniques for manipulating large global datasets and associated model output.

Development of the TEM has progressed in sufficient detail to permit estimation of monthly and annual fluxes of net primary production in South America. The estimates are based on continental-scale datasets of vegetation, soil texture, mean monthly soil moisture, temperature and solar irradiance. Estimates are also based on numerous parameterizations of the model, representing major dryland ecosystems on the continent.

During the past year we have refined the hydrologic component of the DBM for South America with particular emphasis on the Amazon River drainage basin. The model transforms complex patterns of climate into runoff and horizontal transport through the drainage basin. The model was used to test the potential for incorporating global biogeophysical datasets in making regional estimates of fluvial transport. Our work has demonstrated that a relatively simple model, in conjunction with a suite of datasets at 1/2 to 1 degree spatial resolution, can generate reasonable hydrodynamic information over both space and time for use in global modeling studies. Model results mimic observed datasets for both the pattern of runoff generation and the resultant discharge hydrographs. Through sensitivity analysis we also have been able to identify the importance of floodplain inundation on the discharge hydrograph on the mainstem Amazon. To our knowledge this is the first attempt at constructing an integrated "global hydrology model."

Development of the trace gas model has focused on modeling the production, emission and consumption of N_2O from terrestrial soils. A conceptual model which

links N_2O fluxes to TEM and DBM has been developed. In addition, detailed environmental and N_2O flux data have been collected for 37 disturbed and undisturbed sites, and entered into a computerized database. These datasets are of particular importance since they will be used in developing site-specific calibration datasets similar to those used in the terrestrial ecosystem modeling work.

In the coming year, our terrestrial ecosystem work will be focused on making global NPP and heterotrophic respiration estimates. Data from all major dryland ecosystems on the earth have now been collated, the TEM has been calibrated, and we are in the final stages of assembling the requisite global input datasets. We will also mount an effort to simulate wetland ecosystems. As we continue progress on the TEM, we will exercise its ability to quantify the impact of environmental change on the magnitude as well as spatial distribution of potential NPP. We are confident that models such as TEM will prove useful in investigating the impacts of human and climatic disturbance on the biosphere.

We will concentrate on two refinements to the global drainage basin model. The first involves the preparation and testing of a constituent transport model in this next year. We will attempt to encode algorithms for the transport and processing of both dissolved and particulate material. Linkage to the TEM will be a major effort in order to mobilize and transport carbon and nitrogen from the terrestrial landscape into fluvial ecosystems with eventual delivery to the coastal ocean. The effort will necessarily involve the identification and use of candidate conservative tracers. We have also begun a study using the DBM on another large tropical river, the Zambezi located in southeastern Africa. The Zambezi study provides a significant modeling challenge insofar as a series of major engineering works have altered the hydrology of the river. This work is being done in collaboration with the Water Resources Program of the International Institute of Applied Systems Analysis in Laxenburg, Austria.

With completion of the requisite calibration datasets for our trace gas model, we will implement a working model of N_2O gas exchange. Functions are already being developed to describe the effects of major environmental controls (e.g. nitrate and ammonium availability, temperature, soil moisture, labile carbon, soil pH, and soil texture) on the production of N_2O by nitrification and denitrification in the soil. Our aim in the coming year is to attempt to both calibrate the TGM model using site-specific data and to make preliminary geo-referenced estimates in the selected regions.

E. Publications:

Raich, J., D. Kicklighter, J. Melillo, B. Peterson, E. Rastetter, P. Steudler, A. Grace, B. Moore, and C. Vorosmarty, Potential net primary production in South America: test of a global model (in prep).

Rastetter, E.B. et al., A semi-mechanistic approach to modeling biogeochemical responses of the biosphere to global climate change (in prep).

Vorosmarty, C.J., B. Moore, A.L. Grace, M.P. Gildea, J. Melillo, B.J. Peterson, E. Rastetter, and P. Steudler, Continental-scale models of water balance and fluvial transport: An application to South America, Global Biogeochemical Cycles (in press).

Raich, J. and K. Nadelhoffer, 1989, Below ground carbon allocation in forest ecosystems is directly related to above ground production, Ecology, (in press).

Moore B., M.P. Gildea, C.J. Vorosmarty, D.L. Skole, J. Melillo, B.J. Peterson, E. Rastetter, and P. Steudler, 1989, Biogeochemical cycles in Rambler, M.B., Margulis, Lynn, and Fester, R. (eds.), Global Ecology: Towards a Science of the Biosphere, Academic Press, Inc., 204 pp.

TITLE: A Computational Investigation of Reactive Species

INVESTIGATORS: Donald H. Phillips, NASA Langley Research Center
Charles F. Jackels, Wake Forest University

ABSTRACT:

The objective of this task is to determine the thermochemical and photochemical properties of molecular radicals, reaction intermediates, and other short-lived atmospheric species by a computational approach. The techniques used include accurate determination of wave functions, energies, and other properties of reacting molecules and the use of energy derivative methods for the determination of local curvature of potential energy surfaces. Search procedures are utilized to locate transition states and other important molecular structures. The focus is on molecules and reactions which are difficult to investigate with experimental techniques because of short molecular lifetimes or rapid competing reactions.

PROGRESS AND RESULTS:

Several species have received attention during this biennial period.

The higher oxides of chlorine, such as the dimer of chlorine monoxide, are thought to be important in the chemistry leading to polar ozone holes and may provide an answer for an O_2 effect in chlorine-ozone chemistry which has remained unexplained since 1934. For each chlorine oxide chemical formula, there are multiple chemical structures. In the simplest case, ClO_2 , there are $OClo$ and $ClOO$ forms. The latter is almost a conventional compound but the $Cl-O$ bond is quite weak and is not represented well by a simple (single determinant wave function) theoretical description. This appears to be typical of the oxides containing monovalent chlorine (chlorine bonded to only one atom). The hypervalent compounds such as $OClo$ are quite unconventional and obtaining a correct theoretical description of these systems is difficult. During this period, computations to determine the chemical properties of both forms of chlorine dioxide, three forms of Cl_2O_2 , three forms of ClO_3 , one form of Cl_2O_3 , and one form of ClO_4 have been initiated. The initial calculations have been focused on obtaining correct orbitals by use of a multiconfiguration self-consistent field (MCSCF) wave function. Preliminary results on the treatment of hypervalent chlorine compounds were discussed at the 10th Canadian Conference on Theoretical Chemistry, in August 1989.

Investigations of possible complexes between the hydroxyl radical and carbon dioxide have also been initiated. Such complexes would absorb infrared radiation at different wavelengths than uncomplexed carbon monoxide and could, depending upon their concentration, significantly impact greenhouse warming predictions. Two structures have been investigated using self-consistent field (SCF) theory. The first structure has a hydrogen bond between the hydroxyl hydrogen and one of the carbon dioxide oxygen atoms. The SCF binding energy, 2.1 kcal/mole, falls in the expected range. Although the predicted binding energy might increase by as much as 1 kcal/mole if a correlated wave function were used, the binding energy would remain in the weak range. The second structure, which might be described as a protonated carbonate anion structure, is potentially more important. The SCF binding energy is small but the potential increase in binding energy with inclusion of correlation is significant. MCSCF calculations to obtain good orbitals for final correlation calculations are underway.

During this period, work on the CH_3O_2 radical was completed. Calculations to determine the photolysis lifetime of the covalently bonded H_2O_3 complex have been initiated.

PUBLICATIONS:

"Ground and Lower Excited States of Peroxy Methyl Radical: A Computational Investigation," Jawed A. Jafri and Donald H. Phillips, submitted to the Journal of the American Chemical Society.

Upper Atmosphere Data Program (UADP)

Principal Investigator and Institution

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Research Objectives

Rapid, effective access to the increasing volume of information on stratospheric trace gases, both from measurements and model calculations, is important in advancing our knowledge of the Earth's atmosphere. The data have their origins in a variety of sources, ranging from satellite experiments and two-dimensional model predictions to individual balloon measurements, and are found in a variety of locations and formats. This task focuses on development and operation of an electronic data base for such trace gas data. The objectives are to provide effective access to these diverse data sets; to foster electronic data access, manipulation, and display; and to support periodic assessment and intercomparison activities.

Summary of Progress and Results

Over the past 2 years, an operational data base has been implemented from the original data pilot. The software system utilizing the ORACLE data base management system, the Transportable Applications Executive (TAE), the Interactive Data Language (IDL), and specialized Fortran codes has been incorporated. Remote access over the TCP/IP Internet has been added to the existing access over SPAN and via telephone lines. A user base has been established for both general access to public data and private access to proprietary data. Public data sets now include several hundred balloon profiles and LIMS, SAMS, SBUV, and ATMOS satellite data. With advice from the modeling community, a standard latitude and pressure data grid has been established to aid in comparison of different data sets, and the UADP model data and satellite data have been transformed to this grid. Data sets have also been added along with color contour capability.

A major emphasis of the UADP during this period was the support of a model intercomparison activity focused around a workshop held in September 1988. Data from 16 modeling groups around the world were put into the data base for the workshop. The UADP provided the data compilation, access, manipulation, and display services. During the workshop, real time data services were provided both through an on-site workstation and through high speed modem access to the remote UADP computer. Subsequently, updated model data have been incorporated and put onto the standard grid. Graphics of the workshop data, involving over 1600 plots, were generated and included in the workshop report.

Publications

"Conference Proceedings: Two-dimensional Intercomparison Workshop."
Jackman, C., Seals, R. K., Jr., and Prather, M., Editors, in press, 1989.

A. TITLE: Mission and Sampling Analyses for Atmospheric Satellite Experiments

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C. ABSTRACT OF RESEARCH OBJECTIVES:

Orbital analyses, instrument-viewing geometry studies, and sampling simulations are performed to define mission concepts for advanced atmospheric research satellite experiments. These analyses are conducted in collaboration with NASA Headquarters and working groups consisting of atmospheric scientists and experiment developers. Analytical techniques are developed and used to optimize geographical coverage, sensor-viewing geometries, data gathering strategies, sampling schemes, orbital characteristics, satellite launch times, and operational modes of the various experiments and mission concepts. Short-term (7 days) Shuttle missions, the Upper Atmosphere Research Satellite (UARS), and multisatellite missions such as the Earth observing system (Eos) are being studied. Atmospheric experiments which are being analyzed include nadir-viewing sounders, limb-emission scanners, laser systems, and solar-occultation techniques.

D. SUMMARY OF PROGRESS AND RESULTS:

Numerous studies have been performed in the past 2 years in support of experiment and mission development for Earth observations and atmospheric sciences research. A study was conducted to determine science requirements for global climate change studies and for regional climate process studies (ref. 1). Orbital trade-off studies were conducted to identify satellite systems with the temporal resolution necessary for meeting the observational requirements for this research (ref. 2). It was determined that a number of satellite combinations could provide the required coverage. The best combination was 4 sun-synchronous satellites equally spaced in equatorial crossing time. This system would include the proposed NASA polar orbiting platform and similar spacecraft flown by the European Space Agency or by Japan. Other good systems included 2 or 3 sun-synchronous satellites combined with the Space Station Freedom or with a spacecraft in a medium altitude (5200 km) equatorial orbit. High temporal resolution process studies are best accomplished with a geosynchronous platform. The results of these studies were presented at a workshop on Geostationary Earth Observing System Concepts and to the Global Change Technology Initiative Architecture Trade Study Team.

Orbital trade-offs and geographical coverage capabilities were analyzed for the Infrared Limb-sounder Experiment (IRLE) on the proposed Mesosphere Lower Thermosphere Explorer (MELTER) satellite. Latitude coverage during specified seasons was evaluated for a range of scan azimuths with the constraint of avoiding nearly-direct solar views in order to prevent damage to the IRLE instrument (ref. 3). Similar orbital and mission

analysis studies were conducted in support of experiment development for Spectroscopy of the Atmosphere using Far InfraRed Emission (SAFIRE). Geographical coverage capabilities were calculated for the NASA and ESA sun-synchronous Eos satellites. The effects of launch time, season, scan azimuth, multi-azimuth scan modes, and instrument operational scenarios were considered in order to optimize geographical coverage while ensuring that solar viewing constraints are met. Special consideration was given to maximizing polar coverage in the winter hemisphere and, in particular, during October in the southern hemisphere for the purpose of viewing the ozone hole. Study results were included in the successful SAFIRE Eos proposal (ref. 4).

Algorithms were developed and studies conducted to determine coincident measurement opportunities between various types of scanning instruments onboard the Upper Atmosphere Research Satellite and the Shuttle-launched Atmospheric Laboratory for Applications and Science (ATLAS) experiment. The study examined orbital parameters which can be varied in order to optimize coincident measurement opportunities for specified instruments on each satellite. The results showed that a significant number of coincident views from different instruments can be obtained during short-term missions for sensor validation and for analyses involving synergisms between different instruments.

Mission analysis was performed in support of HALOE instrument applications on the UARS. Orbital analyses were conducted to optimize solar occultation coverage for HALOE on UARS for specific launch dates (refs. 5 and 6).

E. REFERENCES:

1. Suttles, John T., Edwin F. Harrison, and Gary G. Gibson: Identification of science requirements for measuring global climate change. Report to the Global Change Technology Initiative Architecture Trade Study Team, August 22, 1989.
2. Harrison, E. F., G. G. Gibson, J. T. Suttles, I. Taback, and J. J. Buglia: Satellite orbit considerations for Earth observation missions. Report to the Global Change Technology Initiative Architecture Trade Study Team, August 22, 1989.
3. A proposal to the NASA to conduct a Phase A study of a Mesosphere-Lower Thermosphere Explorer (MELTER). Hays, Paul B., Principal Investigator; Orbital analysis and IRLE instrument coverage study by E. F. Harrison, 1988.
4. An Eos proposal for Spectroscopy of the Atmosphere using Far InfraRed Emission. Russell, J., Principal Investigator; Orbital analysis by E. F. Harrison, 1988.
5. Harrison, E. F., F. M. Denn, and G. G. Gibson: HALOE geographical coverage for a December 5, 1990 UARS launch. Presented at the UARS/HALOE Science Team meeting. Jan 1988.
6. Harrison, E. F., G. G. Gibson, and F. M. Denn: Further Analysis of Solar Occultation Coverage for a December 5, 1990 UARS launch. Presented at the UARS/HALOE Science Team meeting (also, Memo to Dixon Butler, NASA HQ), February 1988.